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ON A SIMPLE FORM OF APPARATUS FOR DETERMINING THE SPECIFIC HEATS OF SOLIDS AND LIQUIDS WITH SMALL QUANTITIES OF MATERIAL.

BY J. W. MALLET, F. R. S.

Both of the most trustworthy forms of apparatus hitherto in use for the determination of specific heat—those of Regnault and Bunsen—are somewhat troublesome to prepare for an experiment, the latter notably so. Regnault's calorimeter requires a fresh measurement of the water for each occasion of use, and gives accurate results only with considerable quantities of the materials to be examined,* so that in the case of rare substances, of which but a few grams can be had, it ceases to be available. Bunsen's ice calorimeter, beautiful as the instrument is in principle, and capable of being applied to but a fraction of a gram of material, can be repeatedly used within a few hours, or at most days, after it has been packed in snow or shaved ice, but when longer set aside, demands, as has been said, no small care and trouble to get it again ready for use.

An arrangement which shall avoid these disadvantages, which shall be simple, and capable of immediate use after having stood

*Several hundred grams were used in each of a large number of Regnault's own experiments.

aside for weeks or months, which shall work with but little of the material under examination, and which shall give results not necessarily equal in accuracy to the best that may be obtained by more elaborate methods, but accurate enough for the ordinary application to be made by the chemist of a knowledge of specific heat, as bearing on atomic or molecular weight, seems likely to be useful, and may serve to render approximate determinations of this physical constant more frequent, in something the same way that the apparatus of V. Meyer has facilitated the determination of vapor density.

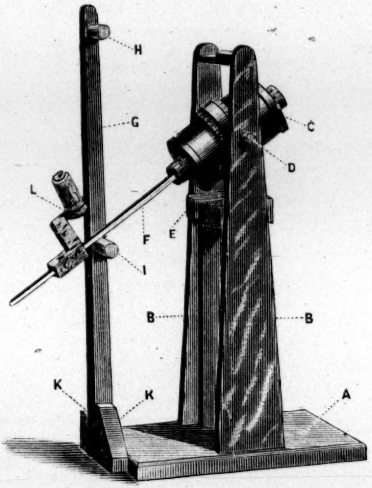


FIG. 1.

Fig. 1 shows in elevation the general appearance of a little calorimeter which I have found to fairly fulfil these conditions; the figure is from a photograph, and of about one-sixth the linear dimensions of the original. The base *A* and two uprights *B B* are made of hard wood. The cylindrical body *C* of the calorimeter is mounted upon two brass pins *D* passing through the opposite

uprights, so that it can be turned round an axis at right angles to its axis of figure. A cross-piece of wood *E* serves to rest the fingers upon in grasping *C* at the time of use, and elastic bands of india-rubber are stretched across between the uprights to prevent the accidental breaking of the thermometer *F* by violent swinging round of *C*, from which it projects. An upright arm *G* bears upon it two corks *H I*, between which the thermometer moves, and the distance apart of these corks determines the extent of motion of rotation of *C* during use. The arm *G* itself turns on a pin screwed into the end of the base, so that it (*G*) can when necessary be turned back out of the way of the thermometer, which can then move further up or down. Two little blocks of wood *K K*, respectively in front of and behind the lower end of *G*, serve

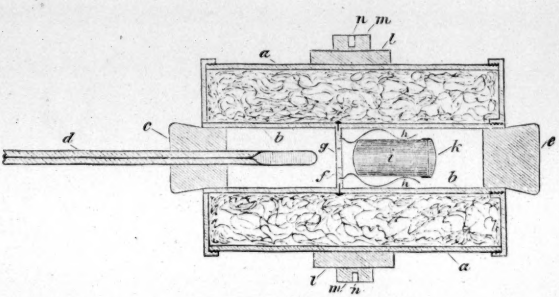


FIG. 2.

as stops to regulate the throwing it into position or back out of the way as required. A reading lens *L* is arranged upon a cork support to slide upon the stem of the thermometer at a proper distance from its scale, and error of parallax is avoided by a short tube above the lens with a small hole in the upper end to sight through.

Fig. 2 presents a longitudinal section of the body (*C* in Fig. 1) of the calorimeter of one-half the real linear dimensions. The outer cylinder *a* is a tube of hard india-rubber (vulcanite),* 105

* This material was selected on the ground of its remarkably low conducting power, a fact which has been strikingly brought out by the comparative measurements of J. Stefan (Wien. Acad. Ber. (2 Abth.); 74, 438–462). He finds, for example, that the true heat-conducting power of vulcanite is several times less than that of ordinary glass, whether considered for equal volumes or equal weights.

mm. long by 64 mm. in diameter inside, 1.5 mm. thick. The ends are round plates of the same material and thickness, and screw down over the extremities of the tube. The inner cylinder *b* is also a vulcanite tube of the same thickness, 22 mm. in interior diameter, passing snugly through a simple round hole in one end plate of the outer cylinder and screwing into a corresponding hole in the plate closing the other end.* The space between the inner and outer cylinders is uniformly but loosely filled with delicate turnings of vulcanite. Both ends of *b* are closed by very accurately fitted corks of the finest texture, free from all hard lumps, flaws, cracks or irregularities of surface. Through one of these corks *c* passes the stem of a mercurial thermometer *d*, specially made for this instrument, the scale bearing centigrade degrees of 6 mm. long, divided to tenths, and reading easily by estimation to twentieths of a degree, the scale running from 5° to 40° outside the cork.† The other cork *e* is solid. The length of the inner cylinder *b* is divided into two unequal parts by a diaphragm *f* of vulcanite of the same thickness with the tube itself, situated 47 mm. from the end bearing the thermometer and 59.5 mm. from the other end. This diaphragm is fixed in its place by three very small screws of vulcanite passing through the wall of the tube, and has in the centre a round hole *g* of 7 mm. in diameter. At three points equidistant from each other round this hole three bits of hard-drawn platinum wire *h*, each 37 mm. long and .35 mm. diameter, are firmly inserted on the side next the unperforated cork, their lower ends curved inward and their free ends sprung apart, so that the little platinum cylinder *i*, when dropped down between them, is grasped firmly enough to retain its place though the tube be inverted, and is supported exactly in the middle of the surrounding space, at equal distances from the inner surface of the tube, from the diaphragm, and from the cork *e*. The platinum cylinder *i*, intended to contain the substance whose specific heat is to be determined, is 28.5 mm. long by 12.5 mm. diameter, stiff

*This inner cylinder might with advantage have been made somewhat smaller, best by shortening both cylinders a little and shifting the diaphragm somewhat toward the end containing the enclosed thermometer.

†As the temperature to which the substance to be examined is raised is determined directly from the boiling point of water under known barometric pressure, the absolute value of the scale of this thermometer, with which the temperature of the mercury in the calorimeter is determined, ought to be known. Comparison with a good standard instrument showed that such errors as exist are too small to sensibly influence the approximate results which alone can be obtained with the apparatus under notice.

enough, and slightly drawn in at the open end, so as to be securely closed by the cover *k*, while the two together weigh only a little over 6 grams. The supporting platinum wires weigh about .5 gram. A ring of cork *l*, 28 mm. wide and 5 mm. thick, encircles the outer cylinder *a* at the middle of its length, and is itself firmly grasped by a ring of hard wood *m*, 12.5 mm. wide and 5 mm. thick, in which, at two opposite points of the circumference, are the holes *n n* entered by the brass pins on which the whole turns. A

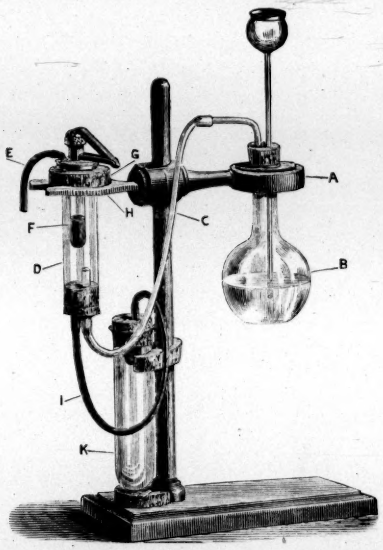


FIG. 3.

weighed quantity of pure mercury—as I have used the instrument, about 220 grams—is placed in *b*, and can be shifted from one division of this cylinder to the other through the hole *g*, as by rotation on the bearings one end or the other is brought uppermost.

Fig. 3—to same scale as Fig. 1—illustrates the mode of heating, to the temperature of a current of steam, the specimen of material

whose specific heat is to be determined. *A* is a ring, sliding on and fixed at a convenient height on the upright rod of a filter stand, by which the flask *B* is supported over a lamp. *B* contains the supply of water for conversion into steam, the steam being carried by the india-rubber tube *C* into the lower end of the large glass tube *D*, from the upper end of which it escapes by the india-rubber tube *E*. The smaller glass tube *F*, closed at the bottom and placed concentrically within *D*, serves to contain the little platinum cylinder holding the specimen under examination. A large ring of cork *G* forms a handle, by which *D* may be taken up without burning the fingers, and during the heating this ring rests on the forked support *H*. The india-rubber tube *I* carries off water as condensed in *D* to the glass cylinder *K*. The tubes *C* and *I* are long enough to allow *D* to be lifted clear of its support and moved a foot or so without disturbing the rest of the apparatus, and without any interruption of the current of steam through *D*.

Fig. 4—to a scale of one-half the real linear dimensions—gives a vertical section of the heating-tube (*D* of Fig. 3) and its appendages. In this figure *a* is the outer glass tube, 145 mm. long and 45 mm. inner diameter, closed at top and bottom by corks *b* and *c*. Through the lower cork pass two bits of glass tube, each of 5 mm. bore, the one connected with the india-rubber tube *d* (*C* of Fig. 3) for the introduction of steam, the other leading to the tube *e* (*I* of Fig. 3), also of india-rubber, intended to drain away condensed water. The small bit of glass tube *f*, also of 5 mm. bore, passing through the upper cork, leads to the india-rubber tube *g*, about 140 mm. long, and serves for the escape of uncondensed steam at such a distance as to avoid any risk of either steam or drops of hot water getting into the calorimeter at the moment of transferring to it the platinum cylinder. The inner glass tube *h* is 15 mm. in diameter inside and 107 mm. long, closed at the lower end, and ground off squarely to a smooth edge at the top. It contains the little platinum cylinder *i* holding the specimen to be heated. After the introduction of this cylinder a loose plug of carded cotton fibre *k* is pushed into the mouth of *h*, which is then closed by a cover or lid formed of a piece of cork *l*, with a smooth lower surface, and carefully fitted so as to come down flat upon the mouth of the tube. *l* is attached to the long arm *m* of a little lever of wood, pivoted in a forked support at *n*, and capable of being very rapidly thrown

over backward by momentary pressure of the thumb on the short arm *o*, thus completely clearing the mouth of the tube *h*. *l* is weighted by a little piece of lead (a flattened buckshot) of 5 or 6 grams imbedded in the cork at its junction with *m*. *p* is a large cork ring, 18 mm. wide and 10 mm. thick, serving as a handle for

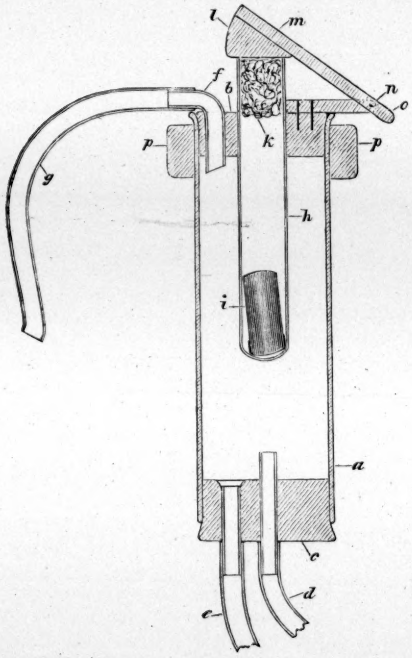


FIG. 4.

a and as a shoulder by which it may rest on the forked support of the stand shown in Fig. 3. An outer jacket of stiff paper, containing cotton fibre or swan's down, may be placed round the glass cylinder *a* during the heating, but this, for the sake of clearness in the figure, is not shown.

The preliminary observations are as follows:—It is first ascertained to what extent the temperature of the mercury in the calorimeter is raised by the metal running down from one end of the inner tube to the other during a given number of turns of the calorimeter on its bearings, the amount of motion in each direction being limited by the distance between the two corks (*H* and *I* of Fig. 1) which the thermometer stem touches at the top and bottom of its arc of movement. The rise of temperature is very small, as may be easily calculated from the extent of fall of the mercury, and is diminished by a part of the heat produced being absorbed by the vulcanite, the platinum and the material of the thermometer. Thus the actually observed rise of temperature was found to be but 0.06° C. for 100 *single* movements of the calorimeter, each transferring the mercury once from end to end of the tube. During this and all other experiments with the calorimeter it is kept in a large room of as steady temperature as possible and free from strong draughts of air.

The little platinum cylinder (*i* of Fig. 2) is now transferred to the bottom of the inner tube of the heating-apparatus (*h* of Fig. 4), in which it rests upside down, the loose plug of cotton wool *k* is inserted in the mouth of the tube *h*, over this the cork cover *l* is brought down, and, the connecting tubes being in position, a lamp is placed under the flask of water and the water boiled actively, but not so violently as to produce difference of pressure inside and outside the heating tube, thus sending a brisk current of steam steadily through the outer tube for half an hour or an hour, preliminary experiments with a small thermometer in the inner tube having shown that this is time enough to bring the contents of the tube closely up to the true temperature of the steam; the difference of temperature between the steam and the material to be heated was never found to be nearly as great as 1° or 2°, observed by Regnault in his experiments. The barometer and attached thermometer are now read, in order to admit of afterward calculating the true temperature of the steam. A few moments before the platinum cylinder is needed, the plug of cotton is quickly withdrawn, the cork cover dropped back to its place, and the current of steam somewhat increased by raising the lamp flame. The calorimeter, which has previously been kept in a part of the room far enough away from the heating-apparatus not to be sensibly affected by it, is now brought near to it, the thermometer is read and the reading

recorded, the arm (*G* in Fig. 1) thrown back out of the way, the cylinder *C*, held lightly but firmly with the left hand, is brought nearly upright, with the thermometer downward, the upper cork (*e* of Fig. 2) loosened in its seat with the right hand so that it may be easily taken out, and then held ready for removal with the thumb and first finger of the left hand. The heating tube (*D* of Fig. 3) is lifted from its support by the cork ring *G*, which is placed as in a fork between the second and third fingers of the right hand, the palm of this hand being upward and the thumb lightly resting on the short arm (*o* in Fig. 4) of the little wooden lever which carries the cork cover *l*. The current of steam is not interrupted while the upper end of the tube (*h* of Fig. 4) is being brought close to the mouth of the calorimeter tube, and then, by quick simultaneous movements with both hands, the cork is momentarily withdrawn from the latter tube, the right thumb is pressed down so as to throw back the cover of the heating tube, and this tube is tilted so as to drop the platinum cylinder down into the calorimeter, where it is held in its central position by the elastic grasp of the three bits of platinum wire. The cork of the open end of the calorimeter is instantly replaced by the finger and thumb of the left hand, and the right hand used to insert it more firmly as soon as the heating tube has been quickly put back upon its support. The calorimeter is now carried back to its place in a distant part of the room, raising as it is carried the thermometer until it is between the two corks of the movable arm *G*, this arm being brought forward into position, and the body *C* of the instrument is gently turned* alternately up and down at such a rate as experience has taught will just allow the complete transfer of the mercury from one division of the tube to the other between the reversals, until the thermometer indicates that the maximum temperature due to the introduction of the heated platinum has been reached. A little practice soon teaches one to guess at about the time necessary for this, and the cylinder may then be stopped for a moment to allow of accurate reading, resuming the motion immediately afterward in order to see whether any further rise of temperature occurs. The loss of heat from the vulcanite is so slow that ample time is afforded for accurate observation of the thermometer. As an additional security, however, against the true maximum temperature being overlooked, it is convenient to have a little detached cylinder of mercury in the ther-

* The projecting part of the solid cork *e* is used as a handle.

mometer tube as an index, like that of the common maximum registering thermometer, but reading from the head of the main column, and using the index merely to assure oneself that the reading is made before the temperature begins to fall. The number of swings made by the calorimeter has been counted as it was turned. A comparison of the initial temperature of the mercury with that finally reached after the introduction of the platinum cylinder, gives the heating effect of the latter plus that due to the agitation of the mercury, as previously determined, for the number of swings made. Subtracting the latter, and after several repetitions of the experiment taking the mean of the results, reduced to the same interval of temperature passed through by the platinum,* the practical effect of the latter in heating the mercury, while itself cooling a given number of degrees, is known.

If now the specific heats of two solid bodies are to be compared, a specimen of each in succession is accurately weighed off, enclosed in the platinum cylinder, raised to the temperature of the steam in the heating apparatus, transferred to the calorimeter, and the effect upon the temperature of the mercury observed, precisely as in the experiment above described with the empty platinum cylinder. Aside from the time occupied in heating up the specimen to be examined, an experiment takes but two or three minutes. It is desirable to take such a quantity of the substance as shall occupy the greater part of the capacity of the cylinder, since otherwise, if the platinum cover be not tightly fitted on, a little mercury may be forced into the cylinder in consequence of the contraction of the enclosed air as it cools down. Good results have been obtained, however, with quantities ranging from .8 gram up to 25 grams. From the heating effect produced in the calorimeter in each experiment is to be deducted that due to the platinum cylinder for the interval of temperature passed through, and to the agitation of the mercury for the number of turns made of the body of the instrument. If the second experiment follow immediately after the first there will generally be little difference between the initial temperatures and final temperatures respectively of the bodies examined, but of course the results are always to be reduced by calculation to the same interval passed through.

To restore the temperature of the calorimeter quickly after an ex-

*The specific heat of platinum, as of mercury, may of course be considered as uniform within the range of variation of the temperatures employed.

periment to that of the room or very near this, a separate cork is provided, to take the place of *e* in Fig. 2, through which passes a sealed test-tube containing mercury. This mercury is cooled a good deal below atmospheric temperature by immersion of the test-tube for a little while in a larger quantity of mercury contained in a beaker and either placed out of doors in cold weather or surrounded by ice water. On inserting the cork in its place at the end of the inner cylinder of the calorimeter, and turning the body of the instrument up and down a few times, the tube of cold mercury reduces the temperature of that which surrounds it until the thermometer reads a little below the temperature of the room. Removing the cold mercury tube and cork, replacing the latter by the solid cork *e*, turning this end of the calorimeter downwards, taking out the thermometer from the other end, to cool it in like manner by immersion of the bulb in cold mercury, and to set the index, and then replacing it, turning the thermometer end down again, taking out the cork *e*, and allowing the instrument to stand for a little while with the inner cylinder open, the temperature of the room is fully recovered.

In no case is the whole heating effect of the platinum cylinder and its contents expended upon the mercury, a portion of the heat going to raise the temperature of the vulcanite, the end corks, the little platinum wires, and the enclosed portion of the thermometer. But the character and quantity of all these substances sharing in the reception of heat being constant, and the circumstances under which heat is given off and received being rendered practically uniform, a large and nearly a constant fraction of the whole heating effect is expended on the mercury, so as to render the results as obtained practically useful measures of the heat given out by the cylinder and its contents. The rate at which heat is taken up from or given off to surrounding matter by the well protected mercury in the calorimeter is so slow, the greatest difference of temperature which need exist between the interior and exterior is so small, and the time necessary for an experiment is so short—but two or three minutes,—that the correction employed by Favre for the rate at which the mercury in his calorimeter was heating or cooling from without during an experiment (obtained from observations before and after) need not be, although of course it might be, applied.

The quantity of the substance taken for examination may conveniently be such as to produce a rise of temperature of the mercury to the extent of 5 or 6, or at most 8 degrees, and if the

specific heat of the substance can be guessed at, or be roughly determined in a first experiment, greater accuracy may be attained by taking such weights of the substance itself and of that with which it is to be compared as shall produce very nearly the same heating effect. If the initial and final temperatures shown by the thermometer be made the same or nearly the same in successive experiments, the correction for the portion of the stem outside the calorimeter becomes constant, and so may be neglected in this merely comparative method. Further, instead of comparing the effect in every case with that of a single standard body, I prefer to take for comparison any substance of which the specific heat is already well determined, and whose general character, as regards specific gravity, conducting power, etc., resembles that of the substance of which the specific heat is to be examined, thus using for the purpose of comparison with substances of analogous character such bodies as platinum, mercury, calcareous spar, sodium chloride, water, benzene, etc. The substances compared should be, as far as possible, in the same state of compactness or subdivision. When a liquid is to be examined the specimen is enclosed in a tube of very thin glass, as nearly as possible filling the platinum cylinder, and with a drop of mercury used to close up the greater part of the space round the side and bottom, the heating effect of the kind and weight of glass used being determined beforehand, and the platinum cylinder with its contents weighed on withdrawal from the calorimeter so as to prove that the little drop of mercury inside has not been increased by any of that in the calorimeter or diminished by any escaping into the latter. Care is to be taken that in all respects, prevailing atmospheric temperature, quickness of manipulation, etc., the conditions of comparison be made as nearly as possible the same. This is rendered easy by the short time required for the experiments.

The two main features peculiar to the little calorimeter now described are simply the employment of mercury instead of water as the liquid to be heated, and the comparison, not of the total amounts of heat given out by different bodies in cooling, but of fractions of the same rendered as nearly as possible equal.

The employment of mercury as the material whose temperature is to be raised by the heat given out by the substance experimented on has certain advantages: 1st. For equal bulks mercury experiences 2.2 times the increase of temperature that water does for the same amount of heat received. The volume of mercury used may

therefore be made quite small while retaining command of sufficiently accurate reading of the change of temperature produced. 2d. The superior conductivity of mercury and its low specific heat facilitate the transfer of heat from the cooling body, shortening the time of the experiment, and thus diminishing the loss of heat through the solid material of the calorimeter, whose properties in the respects mentioned are, as they should be, the reverse of those of the mercury. 3d. Mercury does not sensibly vaporize at such temperatures as are required for the purpose in question, and hence no loss of heat on this account is to be feared. In experiments like those of Regnault, if made with a small quantity of water in an open vessel, the error due to evaporation, and consequent loss of latent heat, may become considerable, or may require for correction troublesome repetition of weighings of the water used. 4th. For the same reason the original quantity of mercury taken remains unchanged, and hence the instrument is always ready for use. To secure this convenient condition, the inner cylinder of the calorimeter is only to be opened with caution, over a little tray of glazed card-board, and any globules, even the most minute, of mercury which may be found adherent to the corks, thermometer bulb, or cold mercury tube, are to be swept together, as is easily done with a small camel's-hair pencil, and returned to the cylinder.

This application of mercury is to be distinguished from that involved in the calorimeter of Favre and Silbermann, and in that recently described by Prof. Stewart* and Messrs. Gee and Stroud,† in both of which the expansion of mercury in the calorimeter itself is directly measured, and used to determine the rise of temperature.

As regards the second peculiarity of the instrument now described, it is obvious that, in any arrangement for measuring the heat given out from one body in cooling by applying it to raise the temperature of another, it is impossible to prevent loss by conduction and radiation, and by making the vessel of material of high conducting power and counting it in with its contents, the difficulty is but shifted from the inside to the outside of its walls. On the other hand, it is clearly not necessary that the whole amount of heat given out by the cooling body be obtained in measurable form; it would come to quite the same thing (as far as the determination of specific heats is concerned) if we could secure the measurement in all cases of a constant fraction of it. It is not pretended that

* Proc. Manchester Lit. and Philos. Soc., March 4, 1879.
† L., E. and D. Philos. Mag., Sept. 1880, p. 171.

this latter result has been fully secured in the apparatus now described, nor is its use proposed as a general substitute for more exact methods, but that it is capable of giving a very fair approximation to such result is, I think, shown by the following examples of determinations of specific heat which have been thus obtained. The figures are not carried in calculation beyond three places of decimals:

A. Substance examined.	B. Substance used for comparison.	C. Spec. heat assumed for substance in col. B.*	D. Spec. heat found for substance in col. A.	E. Spec. heat previously recorded for substance in col. A.*
Silver,	Platinum,	.0323†	.055	.057 (Regnault)
			.058	.056 (Kopp)
			.057	.0559 (Bunsen)
Copper,	"	"	.090	.0951 (Regnault)
			.098	.093 (Kopp)
				.0924 (Wüllner)
Iron,	"	"	.110	.1138 (Regnault.
			.106	.112 (Bunsen)
			.110	
Mercury,	"	"	.032	.0333 (Regnault)
			.034	.0337 (Winkelmann)
			.033	.0334 (Petersson and Hedelius)
			.032	
			.031	
Ferric oxide, (specular iron)	Calcium carbonate, (Iceland spar)	.2073‡	.159	.1669 (Regnault)
			.165	.166 (Neumann)
			.163	.154 (Kopp)
Barium sulphate, (heavy spar)	"	"	.109	.1128 (Regnault)
			.104	.108 (Kopp)
				.1088 (Neumann)
Potassium nitrate, (cryst.)	Sodium chloride, (cryst.)	.2150§	.226	.23875 (Regnault)
			.238	.232 (Kopp)
				.2343 (Neumann)
Cane sugar, (cryst.)	"	"	.298	.301 (Kopp)
			.292	
Ethyl alcohol,	Water,	1.0044‖	.628	.6769 (calc. from Regnault)
			.640	.6138 (Schüller)
			.637	.6273 (Dupré and Page, cor. by Schüller's formula)
				.66885 (calc. from Winkelmann)
Sulphuric acid	"	"	.368	.343 (Kopp)
			.355	.3542 (Pfaundler)

*Where the authorities referred to for the numbers in these columns give the means of ascertaining the spec. heat for the particular range of temperature involved in my experiments, this number is quoted.

†.0323 (Violle) .0324 (Regnault).

‡.2086 (Regnault) .206 (Kopp).

§.2140 (Regnault) .216 (Kopp).

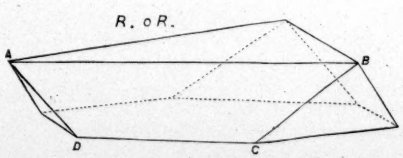
‖1.0039 (Henrichsen) 1.005 (Regnault).

ON JAROSITE FROM A NEW LOCALITY.

By GEORGE A. KÖNIG.

The material is composed of single crystals and crystal aggregations, which rest (for the most part) on a black, brilliant layer of thurgite (hydrohematite). After having ascertained preliminarily the identity of this material with jarosite, I was led to a thorough examination in the hope of establishing the real composition of this compound.

Crystallographical characters.—On some specimens the crystals show a very marked cubical habitus, but one visible corner appearing slightly truncated, inducing me at first to the determination of the mineral as pharmacosiderite. But if this was correct, then the truncation must be a tetrahedron, which I believe had never been noticed on that species. However, when I visited the mine, I found the habitus on most specimens decidedly rhombohedral, with tabular development parallel to the basis, as the accompanying figure shows. Examined with a lens the crystals are very beautiful, and exhibit a remarkable adamantine lustre. But their softness and the strong cleavage present considerable difficulty to any attempt at procuring a crystal fit for measuring. After many failures I succeeded in the separation of a crystal about two millimeters long by one mm. in breadth. (See figure.) From this I obtained the



normal angles for the marginal edge AD=89° 15′ (89° 13′ to 89° 17′).

Basal edge AB=55° 15′ with an uncertainty of ± 4

The pole edge is therefore 89° 15′ and c=1.250. The calculated basal edge is 124° 44′, which agrees very well with the observed mean of 124° 45′.

In Dana's System of Min., 5 edit., the angles are given:

Pole edge=88° 58′; Basal edge=124° 32′; c=1.2584.

This deviation is not inconsiderable, but I have reason to assume that my material is superior to that upon which the latter result was obtained, since Dana says, as a character of the lustre, "dull to a little shining." The lustre of my objective crystals is *adamantine* on the faces and resinous on the fracture, resembling sphalerite very much in this respect. The color is deep reddish brown, rarely yellow in crystals, but generally so for the crusted aggregations; quite transparent; powder light yellow.

Specific gravity=3.144, made upon material under *c*, and consequently not quite correct, but nearly so, since the reduction caused by 2.6 per cent. of quartz is compensated by the increase of 8.67 per cent. of thurgite. The blowpipe reactions are indicated by the composition.

Analyses.—I should have preferred for analysis the fine single crystals, but an attempt furnished such meagre quantitative result that recourse had to be had to the material aggregated into crusts. These were obtained from several specimens, and whilst some appeared very pure, the greater part showed under the lens an admixture of chalcedony and grains of black thurgite. But the jarosite itself was throughout in crystals, not the least massive, and the question whether such material could be relied upon for the solution of a theoretical question had to be answered in the affirmative. For to this end only the ratio between alkali, sulphur and water was necessary. Analyses *a* and *b* are made upon the same sample, which contained only traces of SiO_2; *c*, *d* and *e* were made upon a second sample, which held 2.60 per cent. SiO_2 as quartz.

a. 0.2000 gr. was kept at a bright red heat until the weight remained constant. It gave 0.0664 loss by ignition=32.20 per cent. H_2O+SO_3.

b. 0.2500 gr. dissolved in HCl gave 0.1270 Fe_2O_3.

{ 0.0435 $(K_2Na_2)SO_4$; 0.1005 K_2PtCl_6=0.0356 K_2SO_4.
{ —0.0356=0.0079 Na_2SO_4.

(Determination of sulphur was lost.)

c. 0.5000 gr. gave 0.4190 $BaSO_4$.

{ 0.0640 (KNa)Cl; 0.1840 K_2PtCl_6=0.0561 KCl.
{ —0.0561 KCl=0.0079 NaCl.

0.2550 Fe_2O_3.

0.0130 SiO_2.

d. 0.5000 gr. gave 0.4160 $BaSO_4$.

e. 0.2527 gr. kept at bright red heat until constant weight was reached, 0.0809 loss by ignition = 32.01 per cent. H_2O+SO_3.

In the following table these figures are reduced to 100 after deducting the quartz:

		a.	*b.*	*c.*	*d.*	*e.*
Fe_2O_3	=	...	50.80	52.36	...	...
K_2O	=	...	7.76	7.30	...	...
Na_2O	=	...	1.36	0.90	...	...
SO_3	=	... }	...	29.34	29.32	... }
H_2O	=	32.20 }	...	...	...	32.54 }

Analysis *c* agrees with *b* fairly, being made upon another sample, but it deserves greater credit for accuracy, as it was made upon double the quantity of substance. The two analyses also contain the unknown variable thurgite, and are therefore not comparable. The values obtained under *c*, *d*, *e*, shall be made exclusively the basis in the following calculation. In order to obtain the percentage of water we find the SO_3 in combination with K_2O and Na_2O first, as this was not volatilized by heating.

Then, $32.54 - 29.33 + 6.18 + 1.16 = 10.55$ H_2O; and now,

Fe_2O_3	= 52.36	Fe_2	= 36.65	: 112	= 0.3272		
K_2O	= 7.30	K_2	= 6.06	: 78.4	= 0.0773 }	0.0919	
Na_2O	= 0.90	Na_2	= 0.67	: 46	= 0.0146 }		
SO_3	= 29.33	S	= 11.73	: 32	= 0.3665		
H_2O	= 10.55	O	= 34.78	: 16	= 2.1737		
	100.44	H_2O	= 10.55	: 18	= 0.5861		

$(KNa)_2$	: *c* S	: Fe_2 : O	: H_2O =
0.0919	: 0.3665	: 0.3272 : 2.1737	: 0.5861 =
1	: 3.988	: 3.5604 : 23.64	: 6.377

Now the ratio K_2 : S is absolutely as 1 : 4; some Fe_2O_3 and water being present as thurgite, the empirical formula follows:

$$K_2Fe_6S_4O_{22}+6H_2O.$$

In thurgite there are 4 iron atoms combined with 1 water, hence 0.5604 double atoms with 0.2802 molecule of water, leaving an excess of water of 0.1 molecule. For the analyzed substance we obtain in 100:

(Jarosite)	$K_2Fe_6S_4O_{22}+6H_2O$	= 91.57
(Thurgite)	$Fe_4H_2O_7$	= 8.84
(Excess)	H_2O	= 0.03
		100.44

Thus it is demonstrated, beyond doubt, that jarosite is in form and structure identical with alunite, that in fact both form only *one* species, in which Al_2 and Fe_2 may enter singly or in any proportion, replacing each other.

Rammelsberg* separates jarosite and gelbeisenerz, assuming that the former may have the formula of alunite, adducing Th. Richter's analysis,† which comes near it, if the loss of 1.1 per cent. be added to K_2O. Ferber's analysis‡ is either incorrect or made upon a mixture of jarosite with some other sulphate, and belongs to the indefinite group of "yellow ochre."

Dana combines jarosite with gelbeisenerz into one species, excluding Richter's analysis as "incomplete," for what reason I cannot see, since Rammelsberg gives it as "complete"; but he too remarks that jarosite may have the formula of alunite. It will be well, hereafter, to follow Rammelsberg's precedent and retain the name *gelbeisenerz* for indefinite compounds, in which jarosite probably forms the larger portion; or such analyses as Scherer's, who gives all alkali as Na_2O, for, if this be correct, it makes a new species, from the same reasons which separate jarosite from alunite, *i. e.*, the replacement of one metal for another within the same molecule; but the analysis is probably incorrect. Prof. Benjamin Silliman, Jr.,§ communicated his discovery of jarosite at the Vulture mine, Arizona, without analysis. After the appearance of my analysis of jarosite in the October signature of the Proceedings Academy Natural Sciences of Philadelphia, Professor Silliman kindly sent me a specimen from that locality, which resembles the Colorado mineral very much, but the crystals are much less brilliant and perfect. The professor also states that his analysis, which will be published shortly, confirms my result.

The material for this investigation was collected by myself during the past July. It occurs in a prospect for "carbonates" in porphyry, six miles east of south Arkansas, and two miles north of the river at an elevation of about 600 feet above the latter, in Chaffee County, Colorado. The claim is called the "Iron Arrow." The prospect was made upon the marked iron stain of the rock, the float showing much red ironstone, which is so characteristic of the Leadville formation. Examination convinced me that there is no contact formation here, but many local lenticular masses of thurgite, sometimes of high grade and nearly destitute of phosphorus, but degenerating mostly into a ferruginous hornstone.

* Mineralchemie, 2 Aufl. 1875, p. 2793, f. † B. H. Zg. 1852. ‡ Ibid. 1864. § Am. J. Sc. 1879.

Nearly every piece on the dump showed jarosite. But at no other outcrop showing similar conditions, and there are many, could I find the mineral in central or southwestern Colorado.

UNIVERSITY OF PENNSYLVANIA, *Nov.*, 1880.

ON BEEGERITE, A NEW MINERAL.

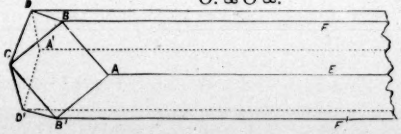
BY GEORGE A. KÖNIG.

The small specimen on which the present investigation was made is seen to be made up of an aggregation of three mineral substances. Probably one half is quartz, in well defined small crystals and grains; the other half consists of a massive light gray mineral, and again of crystals showing a darker gray color, but exhibiting a very strong metallic lustre. Examination proved the chemical identity of the two latter substances, the difference of color resulting probably from the strong reflection of the light from the crystal faces.

Crystallographic symmetry.—The habit of the crystals is orthorhombic after the combination $P\infty \cdot \infty\breve{P}\infty \cdot \infty\breve{P} \cdot \infty\bar{P}$. The crystals are small, so that their faces can only be seen distinctly by means of a good lens, and so grown into groups that single and measurable individuals are very rare. A first trial gave for the zone $P\infty$ the following readings:

0°0′, 43°10′, 70°20′, 113°30′, 125°25′, 180°0′, 250°0′, 305°33′, 348°45′, 360°, but since a close examination shows only 6 faces in the zone, it is clear that images were recorded from other crystals

O. ∞ O ∞.



of the group. Nevertheless one can readily combine the following normal angles: 70°20′, 55°5′, 54°33′, 70°35′, 54°27′, and these agree nearly with the normal angles of the isometric combination O. ∞O ∞. From the same crystal also were obtained normal of edge BD=54°55′; B, D=54°50′. Another crystal was now selected (represented by the figure), and could be so well isolated that the

edges AE, BF, BD, BC and the angle ACA′ were measurable without secondary reflections, giving the following mean of 3 readings:

B′F′ = 55°0′; AE = 70°13′; BF = 54°47′; BD = 54°28′; BC = 54° 20′; angle ACA′ = 90°0′; only the images giving the last angle (ACA) were perfect. However, when the theoretical angles of 70°32′ and 54°44′ were fixed on the goniometer, the strongest light of the undefined images was observed near the cross-hair. The angle of 90°0′ having been measured sharply, there seems to be no reason to doubt the *isometric symmetry* of the mineral, the combination O ∞ O∞ equal being the one most common on galenite. Cleavage is cubical, as strongly as galenite.

Specific gravity was determined on 0.6627 gr. of the mixed minerals in a small pyknometer weighing, when filled with water, 3.5095 gr. Loss of weight = 0.1322; quartz = 0.1703; pure mineral 0.4924. Spec. gravity of quartz being 2.65, the specific gravity of the new mineral is $\frac{0.4924}{0.0677} = 7.273$.

Before the blowpipe the mineral acts like a mixture of galenite and bismuthinite, with a small quantity of copper. It decripitates, and is dissolved by concentrated hydrochloric acid, slowly in the cold, but rapidly in the heated acid. The reactions were made on the pure crystals and on the massive mineral, and found to be identical for both.

Analysis.—By reason of the limited quantity of material, a mechanical elimination of the quartz was not attempted, as quite unnecessary in fact, as it could be accurately estimated in each analysis and subtracted. But in the material of analyses *a* and *b* the massive mineral was excluded as much as possible, while the powder on which *c*, *d* were made contained crystals and massive mineral in about equal proportion.

a. 0.5000 gr. decomposed with hydrochloric acid gave
0.0890 quartz.
0.3832 $PbSO_4$ = 0.2618 Pb.

b. 0.5000 gr. decomposed with conc. nitric acid and potassium chlorate, gave
0.4900 quartz + $PbSO_4$ (extracted with $Na_2S_2O_3$).
0.0930 quartz, and by difference,
0.3970 $PbSO_4$ = 0.2711 Pb.

c. 1.0000 gr. decomposed with HCl and H_2S condensed in an ammoniacal solution of cadmium, gave
0.3106 quartz.

0.4855 CdS = 0.1083 S.
0.1775 basic chloride of bismuth = 0.1420 Bi.
0.6485 $PbSO_4$ = 0.4437 Pb.

d. 0.6400 gr. decomposed with conc. nitric acid alone, gave 0.4720 quartz + $PbSO_4$. The lead sulphate was dissolved by continued treatment with hot nitric acid, and left 0.1955 quartz; hence,

0.2765 $PbSO_4$. The first filtrate being very acid in order to remove all bismuth, a considerable quantity of $PbSO_4$ had entered into it; $Ba(NO_3)_2$ being added, and evaporated to near dryness, the $BaSO_4$ was converted into carbonate by fusion with Na_2CO_3, and from acidulated filtrate the sulphuric acid again precipitated.

0.1486 $PbSO_4$.

0.4251 total $PbSO_4$	in 0 2765 $PbSO_4$	S	= 0.0287
0.2585 $BaSO_4$	...	S	= 0.0355
0.0120 CuO	= 0.008 Cu	S	= 0.0642

(The determination of bismuth in this analysis was lost.)

In the following table these results are calculated in per cent. after deducting the quartz:

	a.	*b.*	*c.*	*d.*	mean.	quotients.
Pb =	63.66	64.60	64.59	64.07	64.23 : 207.2	= 0.309
Bi =	...	...	20.59	...	20.59 : 208	= 0.0990
S =	...	...	15.71	14.23	14.97 : 32	= 0.468
Cu =	...	...	...	1.70	1.70 : 126.4	= 0.013
					101.49	

or very nearly the ratio Bi : Pb : S = 2 : 6 : 9.3.

Pb_6	=	207.2 × 6	=	1243.2	63.84
Bi_2	=	208 × 2	=	416.0	21.36
S_9	=	32 × 9	=	288.0	14.78
				1947.2	99.98

Considering the difficulties connected with the separation of lead and bismuth, the agreement of the results obtained with the calculated percentages must be considered quite satisfactory. The empirical formula of the mineral is therefore

$$Pb_6Bi_2S_9 = 6PbS + Bi_2S_3.$$

This may be regarded as an interesting example of the mass influence on the crystallization of compound molecules.

Whilst the isometric molecule PbS preponderating 6 times, determines entirely the symmetry, the orthorhombic molecule Bi_2S_3 affected merely a prismatic habitus. From the composition it is easily understood that the other properties of this compound coincide nearly with those of galenite. Qualitatively related with the new mineral are the two species cosalite* and schirmerite† described by Dr. F. A. Genth. But the complete absence of silver in the new mineral is very notable.

Schirmerite	=	$(Ag_2Pb)_3Bi_4S_9$.
Cosalite	=	$(PbAg_2)_2Bi_2S_5$.
Beegerite	=	$(PbCu)_6Bi_2S_9$.

Schirmerite has only been found massive, and cosalite in striated prisms of undefined symmetry. But it may be inferred by analogy that both are orthorhombic, because of the preponderance of the orthorhombic Bi_2S_3. Of same molecular structure as beegerite is stephanite, $Ag_{10}Sb_2S_9$, which is so typically orthorhombic, because Ag_2S is here as acanthite orthorhombic, with the orthorhombic stibnite.

The new mineral occurred on the Baltic Lode of the Geneva Mining Company, near Grant Postoffice, Park County, Colorado. I received the only specimen supposed to be in existence from Mr. Hermann Beeger, of Denver, Colorado, and I named the species in honor of this gentleman as a recognition of his services to metallurgy in Colorado.

It may be remarked that the schirmerite occurred on the Treasury lode of the same district.

UNIVERSITY OF PENNSYLVANIA, *Nov.*, 1880.

*Am. J. Sc. 2, 45, 319. †Proceedings Am. Philos. Society, 1874.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

VIII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

THE SYNTHESIS OF ANTHRACENE AND PHENANTHRENE FROM ORTHOBROMBENZYLBROMIDE.*

By C. Loring Jackson and J. Fleming White.

Discovery of Anthracene.

The first notice of anthracene (under the name paranaphtaline) appears in a paper† on compounds of hydrogen and carbon, published by Dumas and Laurent in 1832. They obtained it in the fractional distillation of coal-tar from the portions with the highest boiling-point, but did not succeed in purifying it, as is shown by the melting-point 180°, and the formula $C_{15}H_6$. Laurent,‡ in 1835, studied its oxidation product "paranaphtalese" (anthraquinone), and in 1837 § proposed the name anthracene for it; but neither of these papers, nor one‖ also published by Laurent in 1839, gives a satisfactory account of the hydrocarbon, as the quantity at his disposal was too small for complete purification.

The first accurate characterization of anthracene is due to Fritzsche,¶ who, in 1857, obtained from coal-tar a hydrocarbon with the formula $C_{14}H_{10}$, and melting-point 210°, forming a picric acid compound melting at 170°, but he did not identify it with the anthracene of Laurent. This was reserved for Anderson,** who, in 1861, repeated Laurent's experiments on a larger scale, and showed that his anthracene had the formula $C_{14}H_{10}$, melted at 213°, and was the same as Fritzsche's unnamed hydrocarbon.

In 1867, Fritzsche†† described the preparation of his reagent (dinitroanthraquinone), and its use in the detection and purification of hydrocarbons; and Berthelot‡‡ reviewed all the previous work upon anthracene, determining its boiling-point 360° for the first time.

* Presented to the American Academy. Communicated by the Authors.
† Ann. Chim. Phys. 50, 187. ‡ Ibid. 60, 220. § Ibid. 66, 149. ‖ Ibid. 72, 415.
¶ St. Petersburg Acad. Ber. 1857. Jour. pr. Ch. 73, 286. ** Ann. Chem. Pharm. 122, 294.
†† Zeit. für Chemie, 1867, 289. ‡‡ Bull. Chem. Soc. 8, 231.

The next important paper on the subject appeared in 1869, when Fritzsche,* on account of its behavior with his reagent, pronounced anthracene a mixture of two very similar hydrocarbons, which he called photene, melting-point 210°–212°, and phosene, melting-point 193°.

In the following year (1870) general attention was attracted to anthracene by the appearance of Graebe and Liebermann's famous paper† on anthracene and alizarine, in which they not only proved that alizarine was dioxyanthraquinone by preparing it synthetically from anthracene, but described a large number of derivatives of anthracene, giving for the first time the melting-point of anthraquinone 273°. They showed, too, that Fritzsche's photene was identical with anthracene, but were unable to obtain his phosene, which Barbier‡ four years later showed was probably a mixture of anthracene and phenanthrene.

Syntheses of Anthracene.

In describing the syntheses of anthracene, all those made by the same method will be grouped together, and these groups will be taken up in the order of their discovery.

1. Limpricht§ was the first (in 1866) who made anthracene synthetically, unless, indeed, one of the products obtained by Märcker,‖ in 1865, from the action of heat on tolallylsulphide must be considered anthracenesulphide, but there seems to be no sufficient ground for this supposition. Limpricht's method consisted in heating benzylchloride with water in a sealed tube to 190° for eight hours; the products were benzylether, an oil $C_{14}H_{14}$, and anthracene.

Van Dorp,¶ in 1872, obtained the same result, and proved that the oil $C_{14}H_{14}$, which Limpricht had thought was dibenzyl, is benzyltoluol. Finally Zincke,** in 1874, showed that this reaction resembled that of zinc-dust on a mixture of benzylchloride and benzol, and succeeded in isolating a chloride $C_6H_5CH_2C_6H_4CH_2Cl$ and a complex hydrocarbon. He proved, further, that this synthesis was of little value in determining the constitution of anthracene, since neither anthracene nor benzyltoluol was present in the product of the reaction, but they were formed during distillation by the breaking up of the more complex substances just mentioned.

* Zeit. für Chemie, 1869, 387.
† Ann. Chem. Pharm. Supp. 7, 257. A preliminary notice appeared in 1868, Ber. d. ch. G. 49.
‡ Comptes rendus, 79, 121. § Ann. Chem. Pharm. 139, 308. ‖ Ibid. 136, 94.
¶ Ber. d. ch. G. 1872, 1070. Ann. Chem. Pharm. 169, 207. ** Ber. d. ch. G. 1874, 276.

2. In the year after Limpricht's synthesis was published, Berthelot, in developing his general method for the synthesis of complex hydrocarbons by passing simpler ones through a porcelain tube, heated to redness, obtained anthracene* from toluol (confirmed by Graebe† in 1874), xylol, cumol, and mixtures of benzol with ethylene,‡ and of benzol with styrol; also traces of it by heating acetylene to redness in a glass tube over mercury. The same method was applied successfully by Van Dorp§ to benzyltoluol, that obtained from benzylchloride toluol and zinc-dust, as well as that from benzylchloride and water; by Kramers‖ to phenol (yellow heat); by Claus and Suckert¶ to azobenzol; and by Barbier** to the mixture of toluol with benzol, and to that of diphenyl with ethylene, although the latter yielded only traces of anthracene. Barbier, in 1874, substituted for red-hot porcelain tubes vacuous sealed glass tubes heated to dull redness for a few minutes, and obtained in this way anthracene from benzyltoluol, phenylxylol, diphenylmethane, and liquid ditolyl. While Behr and Van Dorp†† obtained the same result a year earlier by passing liquid benzyltoluol, or liquid tolylphenylketone over gently heated plumbic oxide. The synthesis from orthotolylphenylketone by the aid of heat has been recently repeated by Ador and Rilliet.‡‡

3. The next synthesis of anthracene was published in 1872 by Kekulé and Franchimont,§§ who obtained a small quantity of anthraquinone from the by-products of the distillation of calcic benzoate. Their results were confirmed by Behr‖‖ and Staedel.¶¶

4. Related to this method is that of Barth and Senhofer,*** published in 1873, which consists in heating oxybenzoic acid alone, or with sulphuric acid.

5. In 1873, also, anthracene was first obtained by Zincke's reaction; for, although Zincke††† had not succeeded in finding it, Radziszewski and Zaleski‡‡‡ got it from zinc-dust, benzylchloride and benzol, and Paterno and Filetti§§§ by the action of zinc-dust on a mixture of benzylchloride and phenol; the latter, however, think that it is not formed directly, but by a secondary reaction from the benzylphenol, and this view is supported by a paper published in

* Bull. Chem. Soc. 7, 222. † Ber. d. ch. G. 1874, 48.
‡ Bull. Chem. Soc. 7, 279. § Ber. d. ch. G. 1872, 1070. Ann. Chem. Pharm. 169, 207.
‖ Ann. Chem. Pharm. 189, 131. ¶ Ber. d. ch. G. 1875, 37.
** Comptes rendus, 79, 121, 660, 810. Also, Ann. Ch. Phys. ser. 5, 7, 515.
†† Ber. d. ch. G. 1873, 753. ‡‡ Ibid. 1879, 2298. §§ Ibid, 1872, 909.
‖‖ Ibid. 1872, 971. ¶¶ Ibid. 1873, 178. *** Ann. Chem. Pharm, 170, 100.
††† Ber. d. ch. G. 1873, 137. ‡‡‡ Ibid. 1873, 810. §§§ Gazz. Chim. 1873, 121.

the following year by Zincke and Weber,* who obtained it from a mixture of zinc-dust, benzylchloride and toluol, but suppose that all the anthracene is formed by the breaking up of complex hydrocarbons during the subsequent distillation, in the same way that it is formed from the product of the action of water on benzylchloride. More interesting, therefore, is the synthesis of Piccard,† who obtained anthraquinone by the action of zinc-dust on the chloride of phthalic acid and benzol at 220°.

Under this head should come also the recent experiments of Friedel and Crafts,‡ who, among their beautiful syntheses with aluminic chloride, made anthraquinone from the same mixture, and finally of Ador and Rilliet,§ who, in 1879, obtained it from the chloride of orthotoluic acid, benzol and aluminic chloride.

6. Paterno and Filetti,‖ in a paper published somewhat later, in 1873, describe the synthesis of anthracene by the distillation of benzylphenol with phosphoric pentoxide.

7. In the same year appeared a paper by Grimm,¶ from Baeyer's laboratory, describing the synthesis of chinizarine from phthalic anhydride, hydroquinone and sulphuric acid; while in 1874, Baeyer and Caro** found that phthalic anhydride yielded, with phenol, benzolsulphoacid, anisol, anisic acid, or salicylic acid, either oxyanthraquinone or erythroxyanthraquinone, both of which give alizarine by fusion with potassic hydrate; with pyrocatechin, guaiacol, or protocatechuic acid, alizarine; with hydroquinone (see Grimm), quinic acid, thiochronic acid, or the α and β sulphoacids of hydroquinone, chinizarine. Still later, in 1875,†† they added chlorphenol, boiling-point 218°, to the list of substances which form chinizarine, and converted chinizarine into purpurine by oxidation.

In his last paper‡‡ on phtaleines and their derivatives, published in 1880, Baeyer shows their close relation to the anthracene group, ordinary phthalidine being dioxyphenylanthranol, while a corresponding compound can be obtained from triphenylmethanecarbonic acid.

8. The syntheses of anthraquinone from benzoylbenzoic acid also begin in 1873, when Plascuda and Zincke§§ obtained a little in oxidizing crude benzoyltoluol. In the following year Behr and Van Dorp‖‖ made it by oxidizing tolylphenylketone, and somewhat

* Ber. d. ch. G. 1874, 1153. † Ber. d. ch. G. 1874, 1785. ‡ Comptes rendus, 84, 1450.
§ Ber. d. ch. G. 1879, 2298. ‖ Gazz. Chim. 1873, 251. ¶ Ber. d. ch. G. 1873, 506.
** Ibid. 1874, 968. †† Ber. d. ch. G. 1875, 152. ‡‡ Ann. Chem. Pharm. 202, 36.
§§ Ber. d. ch. G. 1873, 906. ‖‖ Ibid. 1874, 16.

later in the same year converted β-benzoylbenzoic acid into anthraquinone* by heating it with phosphoric pentoxide, a process which ran smoothly and yielded 26 per cent. of the theoretical amount, whereas the para-acid, under the same conditions, gave no anthraquinone whatever. The formation of traces of anthraquinone from the distillation of calcic benzoate alone, and of benzoic acid with phosphoric pentoxide, they ascribe to the previous formation of β-benzoylbenzoic acid. Liebermann† next showed that fuming sulphuric acid produced essentially the same effect as phosphoric pentoxide, converting the β-benzoylbenzoic acid into anthraquinone sulphoacid, and suggested that this method might be of technical value in the future. Rotering and Zincke‡ obtained a similar result by using phosphoric pentachloride, while Thörner and Zincke§ worked out the process further, and showed that chlorine acting on orthotolylphenylketone produced the same effect. Under this head might also be classed the action of hot plumbic oxide on tolylphenylketone already described in Group 2.

9. Closely related to the preceding group is the synthesis depending on the action of zinc-dust on tolylphenylketone, which was studied by Behr and Van Dorp in 1873;‖ and also in 1874,¶ when they proved that the para-compound gives no anthracene, and more recently by Ador and Rilliet.**

Finally, the occurrence of (10) anthracene among the products of the action of potassic nitrite on benzylchloride,†† and of (11) anthraquinone from the oxidation of isatropic acid,‡‡ should be mentioned.

Discovery and Syntheses of Phenanthrene.

It is highly probable that Fritzsche,§§ in 1867, encountered phenanthrene in studying the higher fractions of coal-tar with his reagent, as he describes a hydrocarbon melting near 100°; this observation was entirely overlooked, however, and we owe the first definite statements about phenanthrene to Fittig,‖‖ who announced its discovery in August, 1872; but his preliminary notice of it was so imperfect that Glaser, who discovered it at about the same time, sent it to Graebe¶¶ for investigation as a new hydrocarbon. In 1873 three independent tolerably complete accounts of it appeared

* Ber. d. ch. G. 1874, 578. † Ibid. 805. ‡ Ibid. 1876, 631. § Ibid. 1877, 1477.
‖ Ibid. 1873, 753. ¶ Ibid. 1874, 16. ** Ibid. 1879, 2298.
†† Brunner, Ber. d. ch. G. 1876, 1744. ‡‡ Fittig, Ber. d. ch. G. 1879, 1739.
§§ Zeitschr. für Chem. 1867, 293. ‖‖ Ber. d. ch. G. 1872, 933. ¶¶ Ibid. 968.

almost simultaneously in the *Annalen der Chemie;* these were by Fittig and Ostermayer,* by Graebe,† and by Hayduck.‡

In Graebe's article the synthesis of phenanthrene by passing stilbene or dibenzyl through a red-hot tube is described, whereas Dreher and Otto,§ who tried the same experiment in 1870, before the discovery of phenanthrene, naturally overlooked it.

In the following year Graebe‖ added toluol to the substances which form phenanthrene under these conditions; and Barbier¶ announced that Fritzsche's phosene (see page 384) was a mixture of anthracene and phenanthrene, since he succeeded in getting the characteristic test, brown plates, with Fritzsche's reagent (dinitroanthraquinone) from such a mixture. Armed with this test, he then proceeded to examine the anthracenes from various syntheses, and found phenanthrene in those made by the action of heat on styrol and benzol, ethylene and benzol, benzyltoluol, phenylxylol, and diphenylmethane; also in the anthracene made from benzylchloride by heating with water, and in that from natural alizarine by reduction with zinc-dust; as in all these cases the phenanthrene could not be detected by any other test except Fritzsche's reagent, there seems good reason for receiving these results with caution, especially as he himself has proved by direct experiment** that anthracene cannot be converted into phenanthrene by heat. By passing a mixture of ethylene and diphenyl through a red-hot porcelain tube, however, he obtained a large quantity of phenanthrene, and also by heating liquid ditolyl or stilbene to dull redness in a sealed tube. Finally, Kramers†† found a trace of phenanthrene among the products from passing phenol through a yellow-hot tube.

Constitution of Anthracene and Phenanthrene.

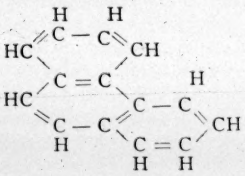
Dumas and Laurent, in their first article on anthracene, considered it a polymerized naphthalene. Anderson, after establishing the formula, called attention to the fact that anthracene and anthraquinone differed from stilbene and benzyl only by two atoms of hydrogen in each case. Berthelot, in 1867, on account of its formation from toluol at a red heat, gave it the formula $C_6H_4[C_6H_4C_2H_2]$,‡‡ which he showed later in the same year was supported also by Limpricht's synthesis, and his own decompositions of anthracene§§ with hydri-

*Ann. Chem. Pharm. 166, 361. † Ibid. 167, 131. ‡ Ibid. 167, 177. § Ibid. 154, 176.
‖ Ber. d. ch. G. 1874, 48. ¶ Comptes rendus, 79, 121, 660, 810; Ann. Chim. Phys. ser. 5, 7, 515.
** Ann. Chim. Phys. ser. 5, 7, 515. †† Ann. Chem. Pharm. 189, 132.
‡‡ Calculated to modern atomic weights. §§ Bull Chem. Soc. 9, 295.

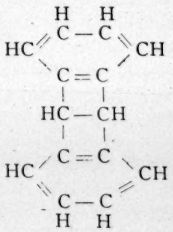
odic acid; he considered it an "acetylodiphenylene," but pointed out the fact that, while the calculated boiling-point of this substance should be 310°–320°, the boiling-point of anthracene is in reality 360°.

In 1870, Graebe and Liebermann proposed two formulas for anthracene, giving the preference to No. 1, on the ground of the syntheses

No. 1.



No. 2.



by Limpricht from benzylchloride, and Berthelot from styrol and benzol; also because this formula is like that of naphthalene, which they show is allied to anthracene in many respects; but these arguments were overturned in 1872 by the discovery of phenanthrene, which not only resembled naphthalene more closely than anthracene did, but yielded diphenic acid and other undoubted derivatives of diphenyl, and was therefore entitled to the first formula, leaving the second for anthracene. This arrangement of the formulas was confirmed by Van Dorp's synthesis of anthracene from benzyltoluol, and by some experiments by Graebe,* which showed that phenanthrenequinone gave diphenyl on distillation with soda-lime, while anthraquinone gave benzol and a very little diphenyl, indicating that there is no direct union of the rings in the latter.

Finally the syntheses from phthalic acid, and the formation of phthalic acid by oxidation, or the action of sulphuric acid† on anthraquinone, established without doubt the ortho position of the connecting atoms of carbon in one of the benzol-rings of anthracene, which was still further confirmed by the syntheses from liquid benzyltoluol and β-benzoylbenzoic acid.

At the end of 1873, therefore, the second formula had been universally adopted as that of anthracene, although the position of the

* Ber. d. ch. G. 1873, 63. † Weith and Bindschedler, Ber. d. ch. G. 1874, 1106.

two connecting atoms of carbon in one of the benzol-rings had not been determined, and the researches of following years, while confirming the points already established, threw no more light on this subject.*

With phenanthrene the case is different, as the proof of the ortho position of the two additional atoms of carbon has not been neglected. In 1878 Schmitz† argued that this was probably the constitution from the fact that diphenyleneketone and diphenylcarboxylic acid were completely destroyed by oxidation; while somewhat later in the same year the point was proved by Schultz,‡ and by Anschütz and Japp,§ almost simultaneously. Schultz did this by converting Griess's metadiamidodiphenic‖ acid (made by the reduction of metanitrobenzoic acid with tin and hydrochloric acid) into diioddiphenic acid, and reducing this to a diphenic acid, which he proved was identical with that from phenanthrene (a proof which he did not make perfectly satisfactory till a later paper,¶ in 1879). Anschütz and Japp oxidized the sodic salt of the phenanthrenesulphoacid with potassic permanganate, and obtained phthalic acid as the only product, whereas, if phenanthrene were not a diortho compound, isophthalic or terephthalic acid must also have been formed.

In 1879 Merz and Weith** proposed a new formula for phenanthrene, $C_6H_4{<}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{>}C_6H_4$, founded on the fact that they obtained invariably perchlorbenzol instead of perchlordiphenyl by the exhaustive action of chlorine upon it; the formation of diphenic acid would then be due to an atomic transformation during the process of oxidation. This hypothesis, however, can hardly be considered as throwing doubt on the constitution of phenanthrene until supported by additional facts, especially since Japp†† has shown by the formation and properties of the β-phenanthrenecarboxylic acid that the C_2H_2 group behaves as if it were part of a benzol ring.

At present, then, the constitution of phenanthrene must be considered as settled, while it still remains to prove the position of the two connecting atoms of carbon on one of the benzol rings in anthracene.

*Anschütz (Ber. d. ch. G. 1878, 1213) made diphenyleneketone by heating anthraquinone with calcic oxide, but proves in the same paper that this reaction cannot be used as an argument in regard to the position of the C_2H_2 group in anthracene.

†Ann. Chem. Pharm. 193, 115. ‡Ann. Chem. Pharm. 196, 1. Ber. d. ch. G. 1878, 215.

§Ber. d. ch. G. 1878, 211. ‖Ibid. 1874, 1609. ¶Ibid. 1879, 235.

**Ibid. 677. ††Ibid. 1880, 573.

Action of Sodium on Orthobrombenzylbromide.

In the hope of settling the constitution of anthracene we have studied the action of sodium on orthobrombenzylbromide, since this might lead to the formation of a hydride of anthracene by the union of two molecules, the side-chain of each being joined to the ring of the other, and of phenanthrenedihydride if the two side-chains and the two rings were united. As these two reactions were likely to take place side by side, we expected that our product would consist of a mixture of these two hydrocarbons.

Orthobrombenzylbromide dissolved in anhydrous ether* was warmed with sodium for some days, fresh shavings of sodium or sodium shot† being added from time to time, until the bright surfaces were no longer tarnished. The greater part of the sodium was then removed, and, after treatment with dilute alcohol to destroy the remainder, the product of the reaction thoroughly washed with water; the yellowish viscous mass thus obtained was oxidized with chromic anhydride, and upon subliming the product, after removing the portions soluble in water and sodic hydrate, yellow needles were obtained which melted at 273°, and gave with zinc dust and sodic hydrate a red color; they were therefore *anthraquinone.*

0.5745 gr. of the substance gave on combustion 1.7000 grs. CO_2 and 0.2180 gr. H_2O.

	Calculated for $C_{14}H_8O_2$.	Found.
Carbon	80.75	80.67
Hydrogen	3.84	4.21

The anthraquinone was further converted into the bromine compound, which by fusion with potassic hydrate yielded alizarine.‡

A second portion of the orthobrombenzylbromide treated with sodium, and afterward freed from it in the same way, was distilled with steam for a long time, a white substance passed over solidifying in part in the condenser, which was proved to be dibenzyl by its odor, its melting-point 52°, and the following analysis:

0.2435 gr. of the substance gave on combustion with $PbCrO_4$§ 0.8240 gr. CO_2 and 0.1700 gr. H_2O.

* When toluol was used in place of ether, the reaction ran so slowly that even after boiling for several days the sodium was but little affected.

† The sodium shot was made by melting sodium under toluol, and shaking (Wislicenus, Ann. Chem. Pharm. 186, 212). It seemed to be not so effective as thin shavings of sodium.

‡ A preliminary notice of the work up to this point was published, Ber. d. ch. G. 1879, 1965.

§ Owing to the ease with which the substance sublimes, great difficulty was encountered in getting a satisfactory combustion.

	Calculated for $C_{14}H_{14}$.	Found.
Carbon	92.31	92.27
Hydrogen	7.69	7.75
	100.00	100.02

No anthracenedihydride could be found in the distillate with steam, although it was carefully searched for.

The residue left in the flask, after the distillation with steam, was a yellow viscous mass, which can be most conveniently purified after distillation *per se*, as this destroys the greater part of the viscous substances containing bromine, which render the extraction with a solvent toilsome and unsatisfactory. The distillate, which passed over without a pause from 260° to redness, consisted of a solid mixed with oil, and had a very disagreeable rank smell, different from that of the undistilled substance. The less volatile parts of the distillate were easily converted by washing with alcohol and ether into white plates with a blue fluorescence, which melted at 212°, and were therefore *anthracene*. The residue left by evaporation of the alcoholic washings consisted of dibenzyl, a brown viscous substance containing bromine and a small amount of a yellow oil; it was tested for phenanthrene by oxidation with chromic anhydride in glacial acetic acid solution, and treatment of the product, after it had been freed from chromic compounds with water, and from acids by weak sodic hydrate, with warm acid sodic sulphite; the solution thus formed was filtered, acidified with hydrochloric (better nitric) acid, and allowed to stand for some time, when it deposited a yellow precipitate, which melted at 198°, and was therefore *phenanthrenequinone*. For further confirmation it was tested, according to Laubenheimer,* as follows: a little of the substance was dissolved in about 5 cc. of glacial acetic acid, a few drops of toluol, and 8–10 drops of sulphuric acid were added, and the mixture allowed to stand over night. It was then poured into water, which, shaken with ether, imparted to it a deep claret-red color, exactly like that obtained from pure phenanthrenequinone under the same conditions.

In a third experiment 20 grams of orthobrombenzylbromide were treated with sodium for nearly a month in the way already described, but, instead of adding water at once to the product, the organic matter was extracted from the sodium and sodic bromide

* Ber. d. ch. G. 1875, 224.

as far as possible with ether and benzol, in order to avoid the reducing action of the hydrogen set free by water. The residue insoluble in these solvents was finally treated with water, and the small amount of organic matter thus obtained added to that at first extracted. The amount of dibenzyl in this product was notably smaller than in those which had been treated directly with water. In a weighed portion an attempt was made to determine the amount of phenanthrene, by adding picric acid to a strong alcoholic solution, but no crystals of the picric acid compound of phenanthrene separated; the solution was therefore evaporated, and in this way a few red crystals were obtained, which had the form of the compound of anthracene with picric acid, and melted in the crude state near 168° instead of at 170°; the quantity was too small to admit of purification. The formation of the anthracene compound, which is decomposed by alcohol, apparently from an alcoholic solution, can be explained by the supposition that it was not formed until the alcohol had evaporated, leaving the anthracene and picric acid dissolved in the oily impurities. In point of fact, it was obtained by imitating the above conditions; that is, evaporating an alcoholic solution of anthracene and picric acid, to which a few drops of toluol had been added. The experiment would seem to show that phenanthrene as such does not exist in the original product.

To meet the objection which might be urged, that the anthracene obtained in the second experiment was not formed directly by the action of sodium on the orthobrombenzylbromide, but during the distillation of the viscous mass, which resembled the substance obtained by Zincke both from his reaction and the action of water at high temperatures on benzylchloride, another portion was treated with ether and hot alcohol, which removed a yellow oil and left *anthracene* identified by crystallizing in white plates melting at 210°. The yellow oil contained either phenanthrene or its dihydride,* as it gave phenanthrenequinone by oxidation, but we were unable to determine which of these substances was present on account of the small amount at our disposal. We are therefore in doubt as to the way in which the phenanthrene occurs in our product; for, on the one hand, we could not obtain the picric acid compound either from the original product or the yellow oil, while, on the other, a substance crystallizing in plates melting between 170° and 190°,

* Phenanthrenedihydride has never been prepared with certainty, although Barbier (Comptes rendus, 79, 121) thought it was formed by the reduction of phenanthrene with sodium amalgam.

which has appeared more than once in the course of this work as an intermediate product in the purification of the anthracene, yields on oxidation anthraquinone and phenanthrenequinone, and seems therefore to be a mixture of the two free hydrocarbons.

No anthracenedihydride could be found in any of the products, nor have we succeeded in detecting benzyltoluol or ditolyl, although it is highly probable that they were formed in addition to the dibenzyl; but the acids resulting from the oxidation appeared in such small quantities, and so contaminated with a brown impurity formed from the viscous brominated substance, that it was impossible to obtain any definite result from them. The viscous substances, too, containing bromine, which were the principal products of the reaction, have resisted thus far all our efforts to bring them into a form suitable for analysis, but we hope to return to this part of the subject hereafter.

Finally the following quantitative results were obtained:—

Organic product from 20 grs. orthobrombenzylbromide	10.85 grs.
Calculated product if free from bromine	7.12 "
Bromine not removed by the sodium	3.73 "
Bromine in 20 grs. orthobrombenzylbromide	12.88 "
Bromine removed as bromide of sodium	9.71 "
Bromine not removed by the sodium	3.17 "

The "bromine removed as bromide of sodium" was determined by precipitating 7.727 grs. of the wash-water with argentic nitrate, which gave 1.482 grs. of argentic bromide. As the weight of the wash-water was 119 grs. this corresponds to the result given above. The two determinations of the amount of bromine not removed by the sodium agree as closely as could be expected when the losses resulting from the repeated extraction and washing of the viscous organic products are taken into account.

75.4 per cent of the whole amount of bromine contained in the orthobrombenzylbromide was therefore removed by the sodium.

Determination of the Amount of Anthracene by Luck's Method.*—1.04 grs. of the product, oxidized, first with chromic anhydride dissolved in glacial acetic acid, and afterward with an alkaline solution of potassic permanganate, gave 0.158 gr. of anthraquinone,

* Zeitschr. Anal. Chem. 1873, 347; 1874, 251.

corresponding to 0.135 gr. of anthracene, that is, 1.409 grs. from the 20 grs. of orthobrombenzylbromide used, or 19.78 per cent. of the theoretical yield.

Determination of the Amount of Phenanthrene.—2.44 grs. of the original product, oxidized carefully by adding a strong aqueous solution of chromic anhydride to a hot solution of the substance in glacial acetic acid as long as a drop of the oxidizing agent made the liquid boil,* on extraction of the product with acid sodic sulphite and acidification with nitric acid, yielded 0.05 gr. of phenanthrenequinone, which corresponds to 0.0428 gr. of phenanthrene; that is, from 20 grs. of orthobrombenzylbromide 0.190 gr., or 2.66 per cent. of the theory. The amount of phenanthrene actually formed must have been somewhat larger than this, as some of the quinone was undoubtedly destroyed by the chromic anhydride,—in fact, the operation can hardly be called a quantitative one.

From the work described above, it appears that 20 grs. of orthobrombenzylbromide yielded,—

Total organic product	10.850 grs.
Anthracene	1.409 "
	9.441 "
Phenanthrene	0.190 "
	9.251 "
Dibromdibenzyl, or its isomeres, calculated from 3.17 grs. of unremoved bromine	6.738 "
Undetermined, containing phenanthrene, dibenzyl, benzyltoluol, and ditolyl	2.513 "

Summary of Results.

Orthobrombenzylbromide when treated with sodium yields anthracene (identified by its melting-point 212°, the formation of anthraquinone melting-point 273°, and of alizarine; 19.78 per cent. of the theoretical yield); and phenanthrene (identified by the melting-point of its quinone 198°, and by Laubenheimer's test; 2.66 per cent. of the theoretical yield). Certainly part, and probably all, of the anthracene occurs in the free state; no anthracenedihydride could be found. Our experiments leave us in doubt as to the way

* Liebermann and Hörmann, Ber. d. ch. G. 1879, 591.

in which the phenanthrene occurs. Dibenzyl was also obtained, an oil possibly benzyltoluol or ditolyl, and a viscous substance containing bromine.

By this synthesis of *anthracene* from orthobrombenzylbromide, it is proved that the *two connecting carbon atoms are attached to each ring in the ortho position*, and thus the last doubt about the constitution of anthracene is removed.

The synthesis of phenanthrene, while it confirms the ortho attachment of the two additional atoms of carbon, proves nothing either for or against the formula recently proposed by Merz and Weith.

The publication of the preliminary notice of this work, already mentioned, drew out an article from Von Pechmann,* describing work done at about the same time as ours, in which he applies to anthracene the ingenious method contrived by Graebe for determining the constitution of naphthalene as follows: bromorthobenzoylbenzoic acid, prepared by the action of bromphthalic acid on benzol in presence of aluminic chloride, was converted into bromanthraquinone by heating with sulphuric acid, which on fusion with potassic hydrate gave erythroxyanthraquinone, and, as this when oxidized yielded phthalic acid, the conclusion drawn from our experiments that anthracene is a diortho substance is confirmed by his work.

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

VIII.—ON SAUER'S METHOD OF ESTIMATING SULPHUR, AND SOME MODIFICATIONS.

By W. G. Mixter.

Several years ago, A. Sauer† and the writer‡ proposed methods for determining sulphur in coals and organic compounds by burning in oxygen and oxidizing the sulphur dioxide with bromine.

* Ber. d. ch. G. 1879, 2124. † Fres. Zeit. 12, 32. ‡ Am. Jour. Sci. & Arts, 3d series, 4, 90.

The former passed the products of combustion through two U tubes containing a hydrochloric acid solution of bromine, and the latter burned in a confined volume of moist oxygen and a little bromine vapor. The writer stated that experiments made by passing the products of combustion of sulphur compounds through nitric acid failed to give satisfactory results. A variable loss was due to a dense white fume containing sulphuric acid, which was not completely absorbed by water or by caustic alkalies. It was mentioned that the apparatus employed was designed to avoid this source of error.

With the hope that Sauer's method or some simple modification of it would give satisfactory results, the following experiments have been made. For the burning of volatile substances, Sauer's plan of a doubly perforated rubber stopper in the anterior end of the combustion tube did not seem desirable, as some sulphuric acid is liable to condense with the water against this stopper; or in case little water is present, some strong sulphuric acid may come in contact with the rubber; hence oxygen was passed through the small hard glass tube *a*, fig. 1, to *c*. Carbonic acid or air was passed in very

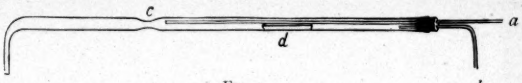


FIG. 1.

slowly through *b* during the volatilization of the assay to prevent the condensation in the cold anterior end of the combustion tube. After all volatile matters had burned, the rubber tubes, connecting with the oxygen and carbonic acid supplies, were closed by clamps and reversed, so that on opening the clamps oxygen passed through *b*, and a very slow current of carbonic acid through *a*. The products of combustion were passed through two U tubes, such as figured by Sauer, containing a solution of bromine in a mixture of one part of fuming hydrochloric acid and two parts of water. In order to find whether the cloud which issues from the U tubes contains sulphur, it was passed by means of a glass tube to near the bottom of an eight-litre bottle. This cloud or fume usually has a well defined surface, which seldom rises above the middle of the bottle. After the cloud completely subsided, the bottle was rinsed three times with water, and the sulphur was precipitated as barium

sulphate. Sauer's plan for non-volatile substance was tried, with the addition of the large bottle above described. In all the experiments the rinsings of the combustion tube were added to the solutions from the U tubes.

	I.	II.
Pure sulphur taken . .	0.2010	0.2638
Total sulphur found . .	99.69 per cent.	99.85 per cent.
Sulphur found in bottle .	0.89 "	0.25 "
Time of burning . . .	1 hour.	15 minutes.

About four times as much oxygen and carbonic acid were used in I as in II.

	I.	II.
Coke	2	2 grams.
Total sulphur found in gaseous products	0.79 per cent.	0.78 per cent.
Sulphur found in bottle .	0.13 "	1.17 "

In order to find whether there is any loss of sulphur in estimating it by this method in substances like coke, a mixture of sugar charcoal and pyrite, FeS_2, containing a known amount of sulphur,* was tried.

	I.	II.
Charcoal	2 grams.	2 grams.
Pyrite	0.2258 "	0.2057 "
Sulphur calculated	0.1199 "	0.1092 "
Total sulphur found	0.1198 "	0.1091 "
Sulphur found in bottle . .	0.0131 "	0.0099 "

The results show that in I, 99.91, and in II, 99.90 per cent. was found of the sulphur taken, and that 11 per cent. in I and 9 per cent. in II passed into the large bottle. No sulphur was found in the residue in the tray. The time of the actual burning of each of the assays was about three-quarters of an hour.

In the two following experiments the products of combustion were passed through 75 cc. of fuming hydrochloric acid, saturated with bromine, distributed in three bulbs of an absorbing apparatus, each

* The pyrite was treated with cold nitric acid, and the whole was kept cool in water, and by constant agitation until only finely divided sulphur remained. On heating in a water-bath the sulphur disappeared and a complete solution resulted. The excess of acid was evaporated, the sulphur was precipitated as $BaSO_4$, the precipitate was fused with sodium carbonate. The fused mass was washed and the sulphur was reprecipitated in the acidified filtrate.

	I.	II.	
Pyrite taken	0.3230	0.3165	mean.
Per cent. sulphur found	53.14	53.08	53.11

bulb having a capacity of 200 cc., and so arranged that the gases bubbled through the liquid in each bulb and finally passed into the large bottle. The apparatus was made entirely of glass to avoid any question of sulphur from rubber connections. The burning in each test occupied about three-quarters of an hour. The results show that about two parts in one hundred parts of sulphur used were not absorbed by the bromine solution.

Charcoal	2	2	grams.
Pyrite	0.2058	0.219	"
Sulphur found in bottle	0.0018	0.0023	"

A hydrochloric acid solution of bromine is probably a no better absorbent of sulphur dioxide than bromine water, and is objectionable for the reason that the excess of hydrochloric acid must be evaporated so that some barium sulphate may not remain dissolved. Bromine water with a cubic centimetre or two of undissolved bromine, in a common two-bulb U tube, loses bromine rapidly when gas bubbles through it, but when the liquid bromine mixes gradually with the water, the passing gas removes the bromine slowly. In the two following experiments, a four-bulb U tube with two bulbs on the bottom was used. Two cubic centimetres of bromine were placed in the lower bulb next to the combustion tube, and sufficient water was added to trap three of the bulbs. It was necessary to shake the U tube occasionally during the combustion in order to keep bromine distributed through the water. The large bottle was used as before. A trace of sulphur found in the residues in the tray was weighed with the total sulphur. The time of actual burning was about three-quarters of an hour.

	I.	II.	
Charcoal	2	2	grams.
Pyrite	0.2024	0.2087	"
Sulphur calculated	0.1075	0.1108	"
Total sulphur found	0.1071	0.1108	"
Sulphur found in bottle	0.0062	0.0026	"

These figures show that 99.63 and 100 per cent. of the total sulphur taken was found, and that 5.77 and 2.35 per cent. respectively condensed in the large bottle, and also that bromine water may replace a hydrochloric acid solution of bromine.

After experimenting with various forms of U tubes, designed for keeping bromine distributed through the water during the passage

of the gases from the combustion, the bulb tube *A*, shown in fig. 2, was found suitable for this purpose. It is about 30 cm. long and 20 cm. high, and is narrowed at the necks so that small rubber stoppers may be used. The enlarged part represents the full size of this portion of *A*. The slight elevation in the glass at *d* is to keep the liquid bromine, shown at *f*, from passing into the narrowed part *e*. A description of the manner of using this absorbing tube will make clear the reasons for the shape at *d* and *e*. It is first connected with the combustion tube *c*, and a cubic centimetre of bromine is poured in and then water added to fill it to the bulbs and the narrow glass tube *g* is adjusted. This tube *g* dips under a

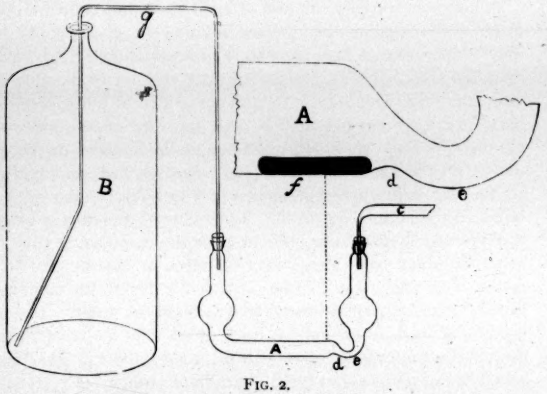


FIG. 2.

little water in *B*. *A* is then slightly inclined so that bubbles of gas from the combustion may slowly pass the lower limb. From time to time, as bromine disappears from the surface of the water, *A* may be inclined more so that a drop or two of bromine shall enter the narrow part *e*, where the passing gas mixes it thoroughly with the water. The remaining experiments were made in the apparatus above described, and the form of combustion tube shown in fig. 1.

	I.	II.	
Sugar	0.670	1	gram.
Sulphur	0.2028	0.2777	"
Sulphur found	0.199	0.2747	"
Per cent. of Sulphur found . .	98.12	98.95	

In I. a slight deposit of unburned matter remained in the bend of the combustion tube.

0.2783 gram of pure carbon disulphide yielded 83.53 per cent. of sulphur; theory requires 84.20. In another trial with carbon disulphide, free sulphur was found in the bromine water.

The first trial with cannel coal was a failure, owing to too rapid volatilization. A light-colored sticky substance containing carbon and a trace of sulphur was found in the bottle *B*. In a second experiment the combustion appeared to have been complete, and 3.1 per cent. of sulphur was found in the volatile portion of the coal.

The results obtained show that Sauer's method is good if the sulphur which passes the bromine solution is caught in a large bottle. A much smaller bottle than the one used would probably stop all the sulphur, but an eight-litre bottle does not allow a troublesome amount of bromine to escape into the room: 150 cc. of water are sufficient to rinse the bottle. Complete combustion can be insured by volatilizing so slowly that the flame of the burning vapors remains a few millimetres back of the end of the tube delivering oxygen. Sauer's apparatus as modified by the writer, supposing a combustion furnace and gas-holders are at hand, has the advantage of simplicity and fewer connections over the plan proposed by the writer for burning in a confined space. Sauer's method requires double to treble the time for burning, and with volatile substances more care to insure complete burning than the writer's original method.

THE DETERMINATION OF SULPHUR IN SULPHIDES AND IN COAL AND COKE.*

By Thomas M. Drown.

The use of bromine as an oxidizing agent, particularly for sulphur, has become very general in analysis, replacing the stronger oxidizing acids. The object of this paper is to describe briefly the experience which we have gained with this reagent in the laboratory of Lafayette College in the oxidation of metallic sulphides.

* Read before the American Institute for Mining Engineers.

Most of the simple sulphides, as blende, pyrite, etc., when exposed to the combined action of an alkaline hydrate and bromine, and finally to hydrochloric acid, are completely and promptly dissolved. The procedure is as follows: The very finely pulverized mineral is first treated, in a beaker, with a solution of sodium hydrate of a specific gravity of 1.25, and heated; bromine is then cautiously added to supersaturation, and finally hydrochloric acid to acid reaction. If any of the sulphide is not taken up, the same operation may be repeated. It is necessary, however, that the mineral be very finely pulverized. Instead of using the pure bromine, a saturated solution of bromine in potassium bromide may be used with equally good effect.

The process is advantageously simplified by making a saturated solution of bromine in the concentrated alkali. This is done by pouring bromine into a solution of sodium hydrate, of the above given specific gravity, until no more is taken up, and then adding a little of the sodium hydrate solution until the liquid does not give off free bromine. The procedure with this solution is as follows: The pulverized mineral is moistened with, say, 10 cc. of the solution, and heated, then hydrochloric acid added to just acid reaction. Two more additions of the alkaline solution, in amounts of 20 cc. each, are added at intervals of about ten minutes, each addition being followed by hydrochloric acid. The total amount of the alkaline solution (containing the bromine) used is, therefore, 50 cc., and the amount of hydrochloric acid should not exceed that necessary to make the solution acid after each addition of the alkali. The mixture should be kept hot. After the final addition of acid, the contents of the beaker is taken to dryness and heated in an air bath to 110° to 115° C., to render silica insoluble. The dry mass is then taken up by hydrochloric acid, and after filtration the sulphuric acid is precipitated by barium chloride. In a sample of copper pyrites Mr. F. E. Bachman obtained, in duplicate analyses, 34.05 and 34.12 per cent. sulphur; in zinc blende 32.97 and 33.09 per cent. In another sample of blende Mr. P. W. Shimer obtained 32.71 per cent.

This method of determining sulphur I find especially valuable in the analysis of coal. By the treatment of coal as above described results are obtained which agree very closely. The coal, as such, is not attacked, and the sulphur obtained, therefore, represents that existing in the coal as pyrite, and also as soluble sulphates. The

residue left by this treatment has been subjected again to the same process, and yields no more sulphur. On combustion, however, or by complete oxidation, either by oxidizing acids or by fusion, additional sulphur may be obtained, which must represent that combined organically with the coal.

The following are some of the results obtained by Mr. Shimer from bituminous coals by the bromine method. The amount usually taken for analysis was between one and two grams:

Bituminous coals.	Total sulphur by fusion with alkaline carbonates and nitrates.	Sulphur by bromine process.
I.	0.043	0.035
		0.035
		0.035
II.	2.16	1.80
	2.17	1.81
		1.81
		1.83
		1.84
		1.85
		1.87
III.	1.17	0 710
	1.18	0.713
		0.717
IV.	1.48	1.096
	1.49	1.098
	1.50	1.100
		1.100

In comparing the bromine method with others it was found that the treatment with hydrochloric acid and potassium chlorate gave on coals with but little sulphur in the form of pyrite the same results, but on coals with much pyrite the results were decidedly lower than by the bromine method. But too few experiments were tried on this point to be decisive. The action of nitric acid and potassium chlorate depends upon the nature of the coal. Some coals are converted partly into a brown unmanageable solution, and others are oxidized completely to a clear solution. In the latter case, of course, the total sulphur could be obtained.

As was said above, the sulphur obtained by the bromine method represents both the sulphides and sulphates in the coal. The methods ordinarily given for the separate determination of calcium sulphate are faulty. Sodium carbonate readily attacks pyrite, and dilute hydrochloric acid and even water, when heated for some time in contact with pyrite, with access of air, contain notable quantities of sulphuric acid. It would seem, therefore, necessary to dissolve out the calcium sulphate by means of water with the careful exclusion of air.

The determination of the total sulphur in coal by means of fusion with alkaline carbonates and nitrates, or chlorates, I find unsatisfactory, owing, I think, to the large amount of salts in the solution in which the barium sulphate is precipitated. A much better method is to burn the coal in a platinum boat placed in a glass tube in a current of oxygen. The products of combustion may be absorbed by a solution of bromine in hydrochloric acid, or by a dilute solution of potassium permanganate. The latter, I have satisfied myself, gives equally good results with the bromine. It is absolutely necessary, in this process, as originally pointed out by Muck,* that the combustion-tube should be washed out with water after the completion of the combustion, since sulphuric anhydride condenses in considerable quantity in the tube beyond the boat. It is further necessary, of course, to fuse the residual ash with alkaline carbonates to determine the sulphur which has not been volatilized by the combustion.

I have in progress an interesting investigation on the effect of coking on the sulphur in coal, to determine what influence the nature of the sulphur—whether in combination with iron as pyrite or organically combined with the coal—has on its elimination in coking. These results must, however, be reserved for a future communication.

LAFAYETTE COLLEGE, EASTON, PA.

* Zeitschrift analyt. Ch. 14, 16.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

VII.—SULPHOTEREPHTHALIC ACID.

By Ira Remsen and W. Burney.

In an earlier paper entitled "Experiments in the Para-Series," * it was shown that, when sulphamineparatoluic acid is oxidized with potassium permanganate without the addition of an alkali, the product is *sulphoterephthalic acid*. An acid potassium salt and an acid barium salt were prepared and analyzed, and some neutralization experiments were made with the potassium salt. All the results obtained proved unmistakably that the acid is really sulphoterephthalic acid. Still, in view of the unusual character of the reaction, it seemed desirable to examine the product more thoroughly, and to furnish unanswerable proofs of the correctness of the conclusion first drawn concerning it. As the acid under consideration must be tribasic, the attempt was first made to obtain salts the composition of which would prove its tribasic character. Such salts were obtained. Further, to show that the acid cannot be sulphamineterephthalic acid, the formation of which would naturally be expected as a result of the oxidation of sulphamineparatoluic acid, a new method of preparation was employed. Instead of starting from the sulphamine compounds, the sulphonic acid of cymene was itself oxidized, and sulphoterephthalic acid was readily obtained in this way. The details of the experiments are described in this paper.

In preparing sulphoterephthalic acid the directions given in the paper above referred to were closely followed. The quantities of the substances used in the oxidation of sulphamineparatoluic acid were: 15 grams of the acid, 75 grams potassium permanganate and 1500 cc. water in each flask. The mixture was heated on a water-bath for 8 to 10 hours. The acid potassium salt finally obtained corresponded closely to the description already given. After two crystallizations it proved to be pure. Several tests were made for nitrogen by fusing small quantities of the substance with sodium, but no evidence of its presence could be obtained. From a hot

* This Journal, 2, 50.

solution of the acid potassium salt the barium salt was precipitated by means of barium chloride. The salt was well washed out on the filter, and then brought into a beaker and boiled with water, after which it was again filtered and washed. A determination of the water of crystallization of this salt was made and the results agreed with those previously found.

0.9890 gram salt lost 0.0456 gram H_2O at 300°.

This loss corresponds to 4.61 per cent. water, while the formula $C_6H_8\begin{Bmatrix} CO_2H \\ CO_2 \\ SO_3 \end{Bmatrix} Ba + H_2O$ requires 4.51 per cent. H_2O.

Neutral Barium Salt.—A weighed quantity of the above mentioned acid barium salt was placed in a flask with water and some pure barium carbonate. The flask was connected with a test-tube containing lime-water, and the contents then heated. A brisk evolution of carbon dioxide ensued, as was shown by the effervescence and the precipitation caused in the lime-water. Although these facts clearly prove that the salt with which we operated contains acid hydrogen, the solution filtered from the excess of barium carbonate did not yield a salt of constant composition. Thinking that possibly the neutral salt first formed might be decomposed by evaporation of the solution, a weighed quantity of the acid salt was boiled with barium carbonate, the liquid then filtered off, fresh water added and the fresh liquid boiled. These operations were repeated until the filtrate gave but a very slight precipitate with sulphuric acid. The united filtrates were now evaporated to a comparatively small volume, and the amount of barium contained in the liquid determined. The amount found did not, however, agree with that required for the neutral salt. In one case too little was found, in another too much.

These experiments indicate either that the neutral barium salt is very difficultly soluble in water, or that it is easily decomposed by boiling with water. Hence another method for its preparation was tried.

About two grams of the acid salt were placed in a large test-tube with a well-fitting, doubly perforated stopper. A clear, strong solution of pure barium hydroxide was then poured upon the salt, and the tube quickly corked. The salt first passes almost completely into solution, the liquid being only slightly clouded, but in a few seconds a bulky precipitate is formed, and the liquid clears up.

After standing well corked for about an hour, the barium hydroxide was washed out by passing water in through a tube reaching nearly to the bottom of the vessel containing the salt. Great precaution was taken to prevent contact with the air during the washing process. This was continued until the wash-water gave little or no precipitate with sulphuric acid. Then the salt was brought on a filter and further washed with cold water. The salt dried in the air was analyzed.

I. 0.5426 gram salt lost 0.0751 gram H_2O at 275°, and gave 0.3646 gram $BaSO_4$.

II. 0.5468 gram salt lost 0.0760 gram H_2O at 275°, and gave 0.3665 gram $BaSO_4$.

		Calculated.		Found.	
				I.	II.
$(C_6H_3O_7S)_2$	...	486	46.69	...	...
Ba_3	...	411	39.48	39.51	39.41
$8H_2O$	...	144	13.83	13.84	13.88
		1041	100.00		

The analyses show that the substance is the *neutral barium salt of sulphoterephthalic acid*, $\left\{ C_6H_3 \left\{ \begin{matrix} CO_2 \\ CO_2 \\ SO_3 \end{matrix} \right\} \right\}_2 Ba_3 + 8H_2O$. Prepared as above described it is of distinctly crystalline appearance. It is almost entirely insoluble in cold water, and but slightly soluble in hot water.

The great insolubility of the salt explains the lack of success which attended our efforts to obtain it by boiling the acid salt with barium carbonate.

Primary barium salt, $\left\{ C_6H_3 \left\{ \begin{matrix} CO_2H \\ CO_2H \\ SO_3 \end{matrix} \right\} \right\}_2 Ba + 5H_2O$. When the secondary barium salt first obtained is treated with moderately concentrated hydrochloric acid, it dissolves with ease if gentle heat is applied. From this solution there separate on cooling well-formed crystals. These were washed once or twice with a little cold water, then again dissolved in a small quantity of hydrochloric acid, and allowed to crystallize. The crystals thus obtained were washed carefully to remove the last traces of barium chloride. The salt was dried by standing in the air and then analyzed.

I. 0.5360 gram salt lost 0.0674 gram H_2O at 235°, and gave 0.1738 gram $BaSO_4$.

II. 0.5328 gram salt lost 0.0670 gram H_2O at 219°, and gave 0.1731 gram $BaSO_4$.

		Calculated.		Found.	
$(C_6H_3O_7S)_2$	...	490	68.34	...	...
Ba	...	137	19.11	19.07	19.10
$5H_2O$	...	90	12.55	12.57	12.57
		717	100.00		

The preparation of the three barium salts which have been described proves beyond any possibility of a question that the acid with which we are dealing is sulphoterephthalic acid.

The tribasic sulphoterephthalic acid, $C_6H\begin{cases}CO_2H\\CO_2H\\SO_3H\end{cases}$, obtained by oxidizing sulphamineparatoluic acid, $C_6H_3\begin{cases}CH_3\\CO_2H\\SO_2NH_2\end{cases}$, yields the three distinct, well characterized barium salts:

$$\text{Primary salt } \left\{C_6H_3\begin{cases}CO_2H\\CO_2H\\SO_3\end{cases}\right\}_2 Ba+5H_2O,$$

$$\text{Secondary salt } C_6H_3\begin{cases}CO_2H\\CO_2\\SO_3\end{cases} Ba+H_2O,$$

$$\text{Tertiary salt } \left\{C_6H_3\begin{cases}CO_2\\CO_2\\SO_3\end{cases}\right\}_2 Ba_3+8H_2O.$$

For some reason unknown to us the experiments with the potassium salts were not as successful as those with the barium salts.

Neutral potassium salt, $C_6H_3\begin{cases}CO_2K\\CO_2K\\SO_3K\end{cases}$. A quantity of the primary potassium salt, $C_6H_3(CO_2H)_2SO_3K+H_2O$, was dissolved in water and exactly neutralized by means of a solution of potassium carbonate. The solution thus obtained was evaporated to dryness, as several attempts to obtain it in crystallized form gave unsatisfactory results. The salt thus obtained is very easily soluble in water. From very concentrated solutions it separates in the form of white, verrucous masses.

Although the results of the analysis of this salt are not good,

they nevertheless show that it is the neutral potassium salt of sulphoterephthalic acid.

0.4675 gram salt gave 0.3296 gram K_2SO_4. This corresponds to 31.61 per cent. K, while the dry neutral salt requires 32.56 per cent. K.

In order to obtain the secondary potassium salt, $C_6H_3\begin{cases}CO_2H\\CO_2K,\\SO_3K\end{cases}$ a solution of the primary salt was divided into two equal portions. One of the halves was then neutralized with potassium carbonate, and the second half added after the neutralization. On evaporation, the solution, strange to say, yielded a product which proved to be a mixture of the primary and another salt, from which it could not be separated. The first crop of crystals being analyzed, gave results about midway between those required for the primary and for the secondary salts. Thus in one case the dried salt gave 18.62 per cent. K, while the secondary salt requires 24.2 per cent. K and the primary salt 13.8 per cent. K.

Another attempt to prepare the secondary salt proved equally unsuccessful. A weighed quantity of the primary salt was brought into solution, and the exact quantity of potassium carbonate necessary to produce the secondary salt then added. On evaporating the solution thus obtained, the salt which separated was found not to have a uniform composition, and the results of the analyses agreed with none of those required by the three possible salts. The product had, further, the appearance of being a mixture apparently of two salts, one crystallized in well-formed crystals, the other being at best but crystalline. It would appear from these experiments that, while the primary and tertiary potassium salts are stable compounds, the secondary salt cannot exist. It is difficult to see how the primary and tertiary salts can exist independently in the same solution and crystallize out at the same time, yet it appears that this actually does take place. Be this as it may, the existence of the tertiary salt above described furnishes the desired proof of the tribasic character of the acid under consideration.

Action of Phosphorus Pentachloride and Ammonia on Sulphoterephthalic Acid.

In other papers it has been shown that, when phosphorus pentachloride and ammonia are allowed to act successively on

compounds containing a carboxyl and a sulpho-group in the ortho-position with reference to each other, the product does not contain two amide groups, but belongs to the class of bodies which have been designated as *sulphinides*, and of which benzoic sulphinide, $C_6H_4\begin{cases}SO_2NH\\CO\end{cases}$, obtained from orthosulphobenzoic acid, is the simplest example. On treating the dry potassium salt of sulphoterephthalic acid in the manner mentioned, the reactions were found to take place as usual, and a substance was formed which crystallizes in long delicate needles from water. It is difficultly soluble in cold water, more easily in hot. After one crystallization it was found to be pure, and was then subjected to analysis.

I. 0.2880 gram substance gave 32.4 cc. N under 764.4 mm. pressure and at 23°.

II. 0.3566 gram substance gave 0.3669 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}SO_2NH\\CO\\CONH_2\end{cases}$	Found.
N	12.39 per cent.	12.76
S	14.16 "	14.13

These results show that the reaction takes place in a manner analogous to that previously noticed in similar cases in this laboratory. The product instead of being the normal amide of sulphoterephthalic acid, viz., $C_6H_3\begin{cases}SO_2NH_2\\CONH_2\\CONH_2\end{cases}$, is a condensation product of the formula $C_6H_3\begin{cases}SO_2NH\\CO\\CONH_2\end{cases}$. It is the *amide of sulphinidoterephthalic acid.*

Formation of Sulphoterephthalic Acid by Oxidation of Cymenesulphonic Acid.

Any doubt concerning the nature of the substance, which we have called sulphoterephthalic acid, that may arise in consequence of the fact that the acid is a product of the oxidation of a nitrogenous substance, is removed, when we consider another and simpler method of preparation which does not involve the use of a nitrogenous substance. We succeeded after some failures in obtaining

sulphoterephthalic acid by direct oxidation of cymenesulphonic acid. We first endeavored to effect the oxidation by means of chromic acid. For this purpose eleven grams of potassium cymenesulphonate were treated with the usual chromic acid oxidizing mixture. As soon as the temperature of the water-bath in which the flask stood reached 60-70° the reaction began. The flame was then removed, the action continuing, as seen by brisk effervescence of the liquid. As the action became less marked, gentle heat was again applied, and in about an hour more the liquid was heated to boiling over a free flame for three hours. In order to reduce the excess of the chromic acid a little alcohol was added. The mass was then diluted to several times its volume with water, and treated with chalk until neutral. The lime was precipitated exactly from the solution thus obtained by means of a solution of potassium carbonate; the filtrate was evaporated to dryness, acidified with sulphuric acid and extracted with alcohol. A small quantity of an organic potassium salt was finally obtained which crystallized in the form of short needles. This was analyzed with the results here recorded:

I. 0.4308 gram substance lost 0.0522 gram H_2O at 75°, and 0.0535 gram at 280°; and gave 0.1282 gram K_2SO_4.

It will be seen that the water is nearly all given off at 75°, though there is a slight additional loss if the heating is carried above this point to 280°, as it was in our analysis. If we take the result at 280° as representing the water of crystallization, the figures obtained correspond very well with those required for the formula

$$C_6H_3\begin{cases}CH_3\\COOH\\SO_3OK\end{cases} + 2H_2O.$$

	Calculated.	Found.
K	13.48 per cent.	13.36 per cent.
H_2O	12.41 "	12.42 "

A sulphotoluic acid has been obtained by Flesch* in the course of an investigation on the sulphur derivatives of cymene. He obtained it by oxidizing cymenesulphydrate with nitric acid, the HS group being converted into the sulpho-group, and the methyl group into carboxyl. As the acid thus obtained when fused with potassium hydroxide yields an oxytoluic acid identical with that described by von Gerichten† and by Remsen and Hall,‡ and

* Berichte d. deutsch. chem. Gesell. 6, 481. † Ibid. 11, 1586. ‡ This Journal, 2, 54.

which has been called *a*-oxyparatoluic acid, it follows that the sulphotoluic acid of Flesch must be identical with that formed by direct oxidation of cymenesulphonic acid, assuming that the oxidation of the latter acid takes place in the same way as that of cymenesulphamide. Flesch states that the acid potassium salt of his acid contained three molecules of water of crystallization. The corresponding salt of our acid was found to contain only two molecules of water. It is possible that some water may have been given off by simple exposure to the air, as that which was determined was given off very easily at the low temperature of 75°.

It is thus seen that the oxidation of cymenesulphonic by means of potassium pyrochromate takes place as the earlier experiments would lead us to expect. The effect of the oxidation is confined mainly, if not entirely, to the propyl group, the methyl group being protected.

In order to effect the oxidation of the methyl group of sulphotoluic acid, potassium permanganate was used. The acid potassium salt obtained by the oxidation with chromic acid, purified as well as possible by means of crystallization, was dissolved in 400 cc. of water and then nearly neutralized by potassium carbonate, the free acid having been found to interfere with the oxidizing action of the permanganate. A solution of permanganate was then prepared containing 30 grams of the salt in 200 cc. water. One-third of this solution was added to the solution of the sulphotoluate, and the whole heated on the water-bath for about three-quarters of an hour, when it was found to be completely decolorized. 33.3 cc. of the permanganate solution were now added, and the heating continued for an hour and a half to two hours. As no further decolorization of the permanganate took place, the process was stopped and the slight excess of permanganate reduced by means of a little alcohol. The filtered solution was evaporated down to a small volume, allowed to cool and then acidified with hydrochloric acid. A large crystalline precipitate was formed. This was collected and recrystallized, when it was seen to have the same appearance as the acid potassium sulphoterephthalate obtained from sulphamineparatoluic acid. It was analyzed with these results:

I. 0.5339 gram lost 0.0335 gram H_2O at 150°, and gave 0.1533 gram K_2SO_4.

II. 0.5536 gram lost 0.0333 gram H_2O at 150°, and gave 0.1594 gram K_2SO_4.

		Calculated.		Found.	
				I.	II.
$C_8H_5O_7S$	...	245	81.10	...	...
K	...	39.1	12.94	12.89	12.92
H_2O	...	18	5.96	6.27	6.01

The physical properties of the salt taken together with the results of the analyses show conclusively that it is identical with monopotassium sulphoterephthalate. A further proof of the identity is given in the fact that when the solution of the salt is treated with barium chloride, a crystalline barium salt is precipitated which conducts itself exactly like barium sulphoterephthalate already described. And on analysis it was found to have the same composition.

0.5477 gram lost 0.0269 gram H_2O at 300°, and gave 0.3177 gram $BaSO_4$.

		Calculated.		Found.
$C_8H_4O_7S$	...	244	61.15	....
Ba	...	137	34.34	34.11
H_2O	...	18	4.51	4.91

It can then scarcely be doubted that the product obtained by the oxidation of sulphamineparatoluic acid with potassium permanganate in neutral solution, and which has been declared by Remsen and Hall to be sulphoterephthalic acid, is identical with the oxidation-product of sulphotoluic acid, and, as the presence of nitrogen in the latter product is an impossibility, it will, we think, scarcely be claimed in the future that both products of oxidation of sulphamineparatoluic acid contain nitrogen. Of the two methods given for the preparation of sulphoterephthalic acid probably that involving the use of the sulphonic acid of cymene will be found to be the better. Judging from our results there should be no difficulty in preparing the acid in any desired quantity.

VIII.—SULPHOTEREPHTHALIC ACID FROM PARAXYLENE-SULPHONIC ACID.

By Ira Remsen and M. Kuhara.

In view of the results described in the preceding paper, it seemed desirable to complete the chain of evidence concerning the nature of the acid under consideration by preparing it from the sulphonic

acid of paraxylene. Pure paraxylene was prepared synthetically from parabromtoluene and methyl iodide according to the well-known method. On distillation the hydrocarbon solidified in the condensing tube. The pure hydrocarbon was converted into the sulphonic acid by mixing it with an equal volume of fuming sulphuric acid. The hydrocarbon dissolved easily with elevation of temperature. The solution was diluted with water, neutralized with chalk, and filtered. The potassium salt was made by precipitating with a solution of potassium carbonate. The calcium carbonate was filtered off and the filtrate evaporated to dryness.

Advantage was taken of the experience gained in connection with the oxidation of cymenesulphonic acid, it having been found that the conversion of cymenesulphonic acid into the substituted terephthalic acid is best effected in two stages. Paraxylenesulphonic acid in the form of the potassium salt was treated with chromic acid, the amounts of substances used being: 30 grams salt, 80 grams potassium pyrochromate and 120 grams sulphuric acid diluted with three times its volume of water. The oxidation was complete after boiling for three hours and a half. The whole was diluted with water, treated with chalk to remove chromic oxide and the excess of sulphuric acid, and then evaporated to dryness. The sulphotoluic acid was obtained in the form of the potassium salt.

The potassium sulphotoluate was then further oxidized with potassium permanganate. The amount of salt used was that obtained by exactly neutralizing 17 grams of the acid potassium salt with the carbonate. To this quantity, dissolved in 600 cc. water, were added 100 cc. of a solution of potassium permanganate, prepared by dissolving 30 grams of salt in 200 cc. water. The reduction was completely effected by heating for half an hour on the water bath. Then 10 cc. of the permanganate solution were added, and the heating increased until this quantity was reduced, and so on. It was found that the total quantity of permanganate necessary to effect the oxidation was 24 grams, and the time occupied was about five hours. The precipitate of hydroxides of manganese was filtered off, the filtrate evaporated to a small volume and hydrochloric acid added. A crystallized salt separated which resembled the known acid potassium sulphoterephthalate in appearance. This was recrystallized a few times, but could not be obtained in pure condition. A small quantity of a salt richer in potassium than the sul-

photerephthalate seemed to be present. Owing to the difficulty experienced in getting the potassium salt in pure condition, we concluded to convert it into the well-known barium salt. The potassium salt was dissolved in water and barium chloride added to the solution. A precipitate was formed which increased in quantity and became more crystalline in appearance on boiling. The precipitate thus formed conducted itself in every respect like the barium salt of sulphoterephthalic acid formed under like circumstances. The analyses of the salt gave the results here recorded.

I. 0.2448 gram salt lost 0.0112 gram H_2O at 290°, and gave 0.1048 gram $BaSO_4$.

II. 0.1856 gram salt gave 0.1072 gram $BaSO_4$.

III. 0.302 gram salt lost 0.0138 gram H_2O, and gave 0.1745 gram $BaSO_4$.

		Calculated.		Found.		
				I.	II.	III.
$C_8H_4O_7S$	...	244	61.15	...	...	...
Ba	...	137	34.34	33.82	33.95	33.97
H_2O	...	18	4.51	4.57	...	4.56
		399	100.00			

These results agree, as will be seen, with those required by a substance of the formula, $C_6H_3\begin{cases}CO_2H\\CO_2\\SO_3\end{cases}Ba + H_2O$, which is that of the *primary barium salt of sulphoterephthalic acid.*

In a recent communication* Jacobsen and Lönnies describe an acid obtained by them by oxidizing sodium α-metaxylenesulphonate with an excess of potassium permanganate. A careful study of this product, which the authors call α-sulphoisophthalic acid, will undoubtedly show that it is identical with the sulphoisophthalic acid first described by Remsen and Iles,† and obtained by them as a result of the oxidation of sulphaminemetatoluic acid. Mr. R. D. Coale is engaged in this laboratory in making a thorough comparison of the derivatives of sulphamineisophthalic and sulphoisophthalic acids. It has already been found that the salts of the two acids differ very markedly, and many of them crystallize well. As a necessary part of the investigation, sulphoisophthalic acid will be made by the oxidation of metaxylenesulphonic acid. From the

* Berichte d. deutsch. chem. Gesell. 13, 1556. † This Journal, 1, 121.

statements thus far made by Jacobsen, it is impossible to say positively whether he has ever really had the derivatives of sulphamineisophthalic acid in his possession or not. If the statement made by him* is correct, that the salt called by him potassium sulphamineisophthalate gives no evidence of the presence of nitrogen when tested by Lassaigne's method, then it is absolutely certain that he did not have the sulphamine acid, for this gives the reaction for nitrogen without difficulty. On the other hand, we must not forget the remarkable fact that this body, in which the delicate test of Lassaigne can not detect the presence of nitrogen, gives up its nitrogen in the form of ammonia, and that the amount of nitrogen in the body which undoubtedly contains none has thus been determined by Jacobsen.† It being thus impossible to decide what substances Jacobsen has obtained, it will of course be impossible to use his results to aid in clearing up the character of the reactions which take place when sulphaminemetatoluic acid is oxidized under different conditions with potassium permanganate. This whole subject will be treated in a later paper, when it will be shown that everything that has been claimed in the earlier papers of this series is only confirmed by later work.

It seems desirable, however, in this connection to call special attention to this fact, that the reactions which have been described in connection with sulphaminemetatoluic acid, and which Jacobsen, by the aid of incomprehensible experiments, has attempted to show were erroneous, are repeated in connection with sulphamineparatoluic acid. It is proved, beyond the slightest doubt, that when *sulphamineparatoluic acid* is oxidized in neutral solution, it is converted into *sulphoterephthalic acid*, whereas, when the potassium salt is oxidized, or enough potassium hydroxide is added to neutralize the free acid, the product is the peculiar nitrogenous anhydride which has been called *terephthalic sulphinide*.

JANUARY, 1881.

* Berichte d. deutsch. chem. Gesell. 12, 2317. † Ibid. 11, 1532.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(Continued from p. 268.)

MATERIALS AND PROCESSES CONNECTED WITH THE CONSTRUCTION OF BUILDINGS.

Chief Building Materials for External Use: Stone and Brick.

Progress has been made in the manufacture of artificial stone, both as to the character of the material turned out and the scale upon which it is used. The first practically successful method of production was that of the original Ransome patent, but it involved heavy consumption of fuel in baking the blocks moulded from sand and solution of sodium silicate, with more or less defacement of the surface of the blocks by smoke. It has been generally replaced by the use of hardening solutions, chiefly that of calcium chloride, applied at ordinary temperature to the mass of silicious sand and soluble glass. One of the most interesting and valuable improvements is that by which the so-called "Victoria stone" is made. Blocks of concrete are moulded from hydraulic cement of good quality, and when dry these are immersed in a solution of sodium silicate, in which has been placed a quantity of silica in easily soluble form, usually of infusorial origin. This calcareous concrete is gradually hardened by the formation of calcium silicate, while the alkali liberated from the solution attacks and dissolves fresh portions of silica, a very limited quantity of soda thus becoming the carrier for a large amount of silica transferred to the hardening block. The process is economical, and diminishes the tendency to unsightly efflorescence of alkaline salts on the surface of the stone when used. The principle of forming by precipitation from successively applied solutions an insoluble silicate or aluminate with which to close the pores of natural stone, and so reduce the effect of weathering, has of late years been employed with moderate success in preserving the walls of public buildings; but, although the principle itself is sound, the difficulty of really penetrating the stone to any considerable depth with the solutions has tended to limit materially the practical value of the process. The manufacture of enormous blocks of concrete, sometimes of 250 or 300 tons in weight, to be lifted bodily from the place of their production and by means of floating derricks lowered to their positions in the foundation of sub-aqueous works, is a comparatively novel applica-

tion of artificial stone, but involves questions of engineering management only, there being nothing new in the chemical aspect of the production of the blocks themselves. To a small extent iron furnace slag, cast into rectangular blocks as it flows from the furnace, has been brought into use as a building material instead of stone.

Probably the most notable change in the practice of brick-making has consisted in the widespread substitution of dry moulding under heavy pressure for the ancient method of moulding the clay with water enough to form a soft dough. The great saving of time arising from the bricks as moulded being at once ready for the kiln, coupled with the saving of space required for drying, reduction of labor in handling the bricks upon the drying yard, and avoidance of the risk of injury by rain on open yards or expense of sheds to guard against this, constitute very material advantages in favor of the more modern practice. Iron furnace slag, whose use in the form of cast blocks has been noted above, has also been sparingly applied, after crushing, to the manufacture of bricks. Great advances have been made in the production of ornamental tiles and the superior kinds of terra cotta for architectural use, but the improvement has been chiefly on the artistic side of the manufacture in form and coloring rather than in the purely technological direction. Although not strictly belonging to this division of the subject, it may be noted that in fire-proof brick for furnace linings and the like applications, improvement has resulted from the substitution for mixed materials as found in nature, often uncertain and variable in composition, of nearly pure silica (crushed quartz), of alumina in the form of beauxite, and of lime and magnesia in the Thomas and Gilchrist linings for Bessemer converters; these materials being in each case mixed with so much only of foreign matter of opposite chemical character (basic and acid respectively) as shall ensure compactness without fusion in burning.

Lime-burning, Mortar and Hydraulic Cements.

One of the chief modifications of practice in burning lime has been the invention of General Scott, R. E., for producing what is known as "selenitic lime," containing about 5 per cent. of uniformly distributed calcium sulphate, by introducing gaseous sulphur dioxide into the kiln during the burning. Quick and hard setting of the mortar made with this lime, and the possibility of using much more than the usual amount of sand, are the advantages which are reported as attained. It has been ascertained by later experiments that the same results can be obtained by simply adding gypsum to the water used in slaking ordinary lime at the rate of 2 to 5 per cent. on the weight of lime treated. The older Roman cement, made from natural hydraulic limestone, has been to a large extent displaced by the improved and greatly extended manufacture of "Portland cement," the latter obtained by intimately mixing

in carefully regulated proportion, chalk or other calcareous material on the one hand, with clay or other silicious and aluminous matter on the other, carefully calcining and grinding the mixture. Instead of using water enough in mixing the materials to produce a fluid mud or slip, from which a large part of the water was removed by a tedious process of settling, careful grinding with but little water has been brought into use, and the waste heat from the calcining kilns is utilized in drying off the solid mud so obtained, each charge as dried being transferred to the kiln, and during its calcination furnishing heat for drying the next portion. The great extension of demand for hydraulic cement of late years has led to the suggestion of several new materials for this use, amongst which one of those attracting for a while much attention was Sorel's oxychloride of magnesium,* prepared by means of the "bittern" of sea-water, or the mother liquors from the treatment of Stassfurt carnallite, but none of these materials have to any large extent passed into general use. Recently a cement has been introduced by Ransome, made by burning a mixture of lime and pulverized blast-furnace slag, which has been reported upon in terms of high praise. It is said to set much more rapidly than Portland cement, to attain greater absolute hardness, and to be manufactured at less cost.

Stucco.

There have been various small changes announced in the methods of hardening gypsum for casts, mouldings, plastering walls, etc. Alum, as employed in Keene's cement, and borax, as used in making the so-called Parian cement, are probably still the chief materials for producing the hardening effect, which is applied not only to the original white gypsum but also to that with which pigments have been mixed in order to imitate the appearance of marble.

Few inventions in connection with the comfort of our dwellings would have more value than the production of a really satisfactory substitute for plaster on the inner surface of the walls. Such a material should combine lightness, smoothness of surface, moderate porosity, freedom from the brittleness which makes plaster so easily injured, adaptation to the production of decorative effect, capability of being washed, low conducting power for heat, incombustibility—or at any rate considerable power of resisting the progress of fire—and reasonable cheapness. Some of these properties are possessed by the sheets of "muralis" introduced a year or two ago for the purpose in question, which is made by rolling a mixture of linseed oil and ground vegetable fibre on to a strong cotton fabric, but in other respects this invention has not fulfilled the demands of proper wall covering and decoration. The problem is doubtless largely a mechanical one, but involves chemical considerations also.

* Proposed also as a substitute for gypsum in making casts, etc., and as the cementing material in the production of artificial stone.

Preservation of Timber.

For this purpose numerous materials continue from time to time to be proposed. Of late years less extensive use has been made of saline preservatives than of the crude phenols from coal tar, coupled with the external use of coal tar or pitch varnish. Hatzfeld has introduced the use of tan liquor, followed by crude acetate of iron. Experiments by means of hydrostatic pressure, and those of Boucherie, involving the natural capillary action of the sap-bearing vessels of the timber, have led to further progress in the mode of mechanically introducing the preservative fluids of whatever kind into the interior of the wood to be treated. In the light of modern knowledge of the lower forms of life, much value would probably attach to a careful investigation of the direct effect of various supposed poisons upon dry rot, and other moulds and organisms whether belonging to the vegetable or animal kingdom, (including teredo, termite, etc.), which lead to the decay of timber. Hitherto the selection of materials used has been made pretty much on empirical grounds.

Glue and other Cements of various application.

In glue-making it has been shown that needlessly protracted boiling and the use of a high temperature produced by high-pressure steam greatly injure the quality of the product as to strength and adhesiveness. The practice has therefore been introduced with advantage of boiling under pressure equal or superior to that of the atmosphere only until soluble gelatine has been produced, and then boiling down in a vacuum pan until the proper consistence has been reached for solidification in the moulds. It is asserted that bleaching of the scraps of skin, etc., by means of a saturated solution of sulphurous acid before the boiling, not only yields glue of much lighter color and greater clearness and lustre, but also produces a swelling up of the material, probably analogous to that which occurs in the "raising" of hide to be tanned, which materially shortens the time required for boiling into glue. It has also of late been proposed to remove fat from the animal matter by preliminary exhaustion with petroleum spirit in order to facilitate the action of the water in the boiling process.

Among the many minor cements which have been brought into use of late years, a few of those most likely to prove permanently valuable, at least for special purposes, are the following. "Chromated glue," prepared by adding to solution of ordinary gelatine or carpenter's glue chromic acid or potassium pyrochromate, at the rate of about one-fifth the weight of the dry gelatine, this material becoming permanently insoluble in water after it has been used as a cement and exposed to light. Caseine, from curdled milk, dissolved with the aid of borax. Glycerine and well-dried litharge, producing a cement which sets even under water, and is said to resist some of the solvents most difficult to manage, such as ben-

zene and carbon disulphide; the proportions recommended are 50 grams of litharge and 6 cub. centimetres of a mixture of 5 parts by volume of glycerine and 2 of water. Boettger's cement, made with fine precipitated chalk, stirred into solution of sodium silicate at 33° B, to which pigments may be added if desired, the mixture hardening in six or eight hours. The so-called "Spence's metal," a fused mixture of iron pyrites or other metallic sulphides with excess of free sulphur; this material, with a melting point reported as low as 160° C, while presenting a considerable amount of cohesive strength and power of resisting exposure to air and water, with low price, seems worthy of some attention, especially for making the joints of water pipes, etc., although the claims put forward in its behalf on its first announcement were rather extravagant. Although now far from new, the extremely valuable "Marine glue," of Jeffrey, does not seem to be as well known in this country as it deserves. Prepared by dissolving 1 part of india-rubber in crude benzene, and mixing with 2 parts of shellac by the aid of heat, the water-proof character of this cement, in connection with its slight elastic flexibility, the ease with which it is applied when warm, and the promptness with which it sets on cooling, make it a most useful substance in many applications to house construction and furniture, as well as on board ship, where it was originally intended to be chiefly employed.

Pigments for House-Painters' use.

In regard to the most important of these, white lead, there have been several variations of the long used processes of manufacture. Probably the most notable of these is the modern German process, carried out in masonry chambers of considerable dimensions, instead of the small earthen pots of the ancient Dutch method, steam, vapor of acetic acid, air and carbon dioxide being introduced in regulated amounts to act upon thin plates of cast lead. In connection with the processes in which, with a view to extension of surface, lead is used in pulverulent form instead of in plates, may be mentioned the method of pulverizing the metal, patented by Tuttle & McCreary in this country, by means of a jet of high pressure steam driven through a falling stream of molten lead. When pulverulent lead is used for the after manufacture there is always some risk of particles of metal escaping complete corrosion, and, on being ground up, injuring the whiteness of the resulting paint. Pattinson's white oxychloride of lead is, or was very recently, still manufactured, but does not play a very important part in the general supply. Zinc white has grown into much more extensive use than formerly, and the production of the oxide represents a valuable industry. Within the last few years a white oxysulphide of zinc, approximating in composition to 5ZnS.ZnO, has been brought forward, made by precipitating sulphate or chloride of zinc solution with a soluble sulphide, roasting the product slightly at a

cherry red heat, raking out from the furnace into water, grinding finely, and drying. Its beauty of appearance and covering power are very highly spoken of. Mixtures of zinc sulphide with barium sulphate, of generally similar character, have also been placed in the market. The production of lamp-black of great purity and beauty, from the smothered combustion of the natural hydrocarbon gas of the petroleum region, is a comparatively new industry ; this material is, however, too dear for general house-painters' purposes, and is more used for choice printing ink than as a pigment. Among the red colors, lead oxychromate has come to be manufactured pretty largely, as a spurious substitute for and an adulterant of vermilion, and under various trade names as an independent pigment. Red, violet and blue lakes, made with aniline colors, have come into use to some extent. Among blue pigments, the greatest extension of manufacture has occurred with ultramarine, not only as regards the very large quantity now annually turned out, but also the variety of tints obtained, reaching from blue to distinct violet and a tolerable red, as well as the long known green. A paper of last year by Heinze* illustrates the wide variation as to amount of product and cost from the different mixtures of materials in use amongst ultramarine manufacturers.

Of green colors, Guignet's green (chromic oxide) has come to be made more largely and of much greater brilliancy than formerly, but must still be counted among the dearer pigments. Barium manganate has been introduced as a green pigment, and is said to exhibit much greater permanence than might have been expected from its composition.

Vehicles for Paints.

In careful hands the boiling of linseed oil is improved by keeping the temperature down to the lowest necessary point, using steam heat instead of an open fire, though much of the boiled oil of commerce shows the effect of over-heating and needless darkening in color. Manganese borate and other substances have come into use as "dryers," but no very notable improvement in this direction has been announced. Mixed distemper colors have been rendered capable of preservation for some time before use by addition of carbolic acid in small quantity to the animal size. Soluble glass solution has been used to some extent in the production of a kind of emulsion as a vehicle for paints for outdoor use.

Varnishes.

Probably the most noteworthy change in the manufacture of varnishes has been the extension of use of dammar and kauri resin, in the treatment of which, however, much remains to be done in order to secure a thoroughly satisfactory product. The large amount of kauri resin obtainable in New Zealand, and its mode-

* Polytechn. Journ. 231 ; 366.

rate price, render it well worth more careful examination as to its solvents and the conditions under which they should be used. It is said that more information on this subject has already been obtained by certain manufacturers than has been published.

The method of Violette for rendering copal, kauri, etc., more readily soluble by preliminary fusion *in closed vessels* at well-regulated temperature is apparently of real value.

Appendix to Building Appliances.

A.—*Explosive Agents* (*used in blasting and otherwise*).

In the economy of gunpowder manufacture the most valuable improvement known to the writer is that introduced at the Confederate powder mills at Augusta, Georgia, by Col. G. W. Rains, in 1862 or '63, namely, incorporation of the materials by a process of steaming. The sulphur and charcoal were severally pulverized and bolted, the nitre, pulverized by disturbed crystallization, added to these, and the mass, roughly mixed, was moistened with water and introduced into horizontal cylinders of sheet copper 30 inches long by 18 inches in diameter. These cylinders revolved slowly on a common axis consisting of a heavy brass tube 3 inches in diameter, perforated within the cylinders by a number of holes ½ inch diameter. High-pressure steam was introduced through this tube, raising the temperature to the boiling point, while the water produced by condensation, added to that originally used to moisten the materials, reduced them to a semi-liquid slush, which was run out of the cylinders after about eight minutes' rotation. On cooling, this mud became a damp solid cake, the nitre, which in the state of boiling hot saturated solution had entered the minutest pores of the charcoal, now recrystallizing. The cake so produced was transferred to the incorporating mills, and under 5-ton rollers was in an hour brought to the condition of finished mill cake, ready to be cooled and granulated, while without the steaming process four hours' incorporation in the mills had previously been necessary to produce powder of the same first-class character. The capacity for work of the mills was thus practically quadrupled, the thorough saturation of the charcoal with nitre being accomplished by the steaming, while it remained for the rollers merely to complete the mixture of the whole mass and to give the required density to the mill-cake. The enormous increase in the size of ordnance has led to much greater pains being taken in regulating the density of the press-cake made from the crushed mill-cake by hydraulic pressure, and much attention has been given to producing grains, pellets and prisms of finished powder of determinate size and shape. As regards the proportions in which the materials of gunpowder are used, the researches of Noble and Abel have shown that much less difference in the work done on explosion is caused by very con-

siderable variation of composition than would have been previously supposed likely, the production of a higher temperature on explosion being attended with the formation of a less volume (at normal temperature and pressure) of permanent gases, and *vice versâ*.

The investigations of Lenk and Abel have determined the proper conditions for the manufacture, storage and use of gun-cotton, have rendered it a practically manageable explosive, especially in the form of compressed pulp, and one of special value in certain cases. The latest modification proposed in the process of making it is that of Aimé Girard,* who moistens the vegetable fibre to be treated with a very weak solution of sulphuric or hydrochloric acid, heats to 50° or 80° C, or allows the moistened material to stand at common temperature for some weeks, or instead of the liquid acid uses a current of moist gaseous hydrochloric acid, finally washing out thoroughly with water. The "hydro-cellulose" thus formed is acted upon with concentrated nitric acid in the usual way, and a product is obtained which is extremely friable, and which after reduction to impalpable powder is said to resemble dynamite in its simple fusion on contact with flame (?) and in the extreme violence of its explosion by a shock.

In making nitro-glycerol it has been found that the inconvenience and danger resulting from rise of temperature in the mixture may be obviated by first treating the glycerol at 30° C with three times its weight of concentrated sulphuric acid, forming sulphoglyceric acid, cooling, and adding to separately mixed and cooled nitric and sulphuric acid. The reaction is attended with little heating, is not complete until twenty-four hours or so after mixture, and produces a distinct layer of nitroglycerol, to be syphoned off and washed. While dynamite is still largely used, consisting of nitroglycerol given solid form by mixture with inert mineral matter, there have been numerous more or less successful attempts to produce energetic explosives by substituting for such mineral matter (infusorial silica) a solid substance or substances capable of contributing to the production of useful effect. The most interesting of these until recently was the "glyoxaline" of Abel, consisting of ordinary gun-cotton soaked with nitroglycerol, both substances being energetic explosives, and the latter supplying the surplus oxygen which the former needs to render complete combustion possible. To this mixture a still more convenient form has recently been given, the so-called "explosive gelatine" of Nobel, prepared by dissolving about 7 per cent. of photographer's pyroxyline (soluble gun-cotton) in nitroglycerol to a jelly, with which may advantageously be mixed 10 per cent. of the most highly explosive tri-nitro-cellulose. This new material is free from the disadvantage of the nitro-glycerol separating, as from dynamite. For some purposes it is modified by the addition of a little camphor.

*Comptes rendus, 88, 1322, and 89, 170.

Although of subordinate importance, the picrates should be mentioned as comparatively recent additions to the list of standard explosives.

Our general knowledge in regard to the phenomena of explosion has received important additions from the long-continued researches of Abel, Noble, Champion and Pellet, the information obtained having already led to valuable applications in practice, and serving to point out clearly lines for future investigation. Amongst the chief subjects already examined are: the distinction between detonative explosion, developed by sudden mechanical shock (as from a separate initiative explosion), and inflammatory explosion, brought about by the application of a burning body to some part of the explosive material; the effect of complete enclosure within strong walls, or simple surrounding of the explosive with air or other readily mobile material; the conditions of transmission of detonative explosion from one mass to another of the same explosive agent, or from an explosive of one kind to one of different nature; the influence of the physical state and mechanical condition of the explosive; the phenomena of explosion in a mass saturated with or surrounded by water; and the chemical character of the products, the temperature, and the gaseous tension developed under different circumstances of explosion.

B.—*Disinfectants.*

The increased attention bestowed of late years upon sanitary matters has led to the manufacture, on quite a large scale, of numerous materials claiming to be valuable as disinfectants. The real value of these, when genuine, it is not easy accurately to estimate in the present imperfect condition of our knowledge as to the nature of the evils to be combatted and the manner in which they should be attacked. Unfortunately, in too many cases there has been extensive adulteration of substances which in their proper condition might fairly be accepted with some confidence, and in too many cases also there has been ignorance displayed in the use as well as in the choice of materials for this purpose. As a single illustration of the need existing for much fuller investigation of the subject of disinfecting materials and methods, the recent observations of Dianin* may be referred to. It has been generally held that carbolic acid and chlōride of lime, separately useful as disinfectants, should be viewed as "incompatibles," the former liable to be destroyed by the latter, with loss of activity on the part of both. Dianin finds that if these two materials be mixed, tri-chlor-phenol is at once produced with but little of the di- and mono-chlor-derivatives, and that the mixture, representing essentially the calcium compound of tri-chlor-phenol, possesses notably greater antiseptic activity than either of the original substances taken by itself. Among the many individual points calling for

* Chem. Central-Blatt., 3 Nov. 1880, 689; quoting from a Russian journal.

accurate and unbiased scientific investigation, may be instanced the effects producible upon the lower forms of living organisms by very low temperatures, although this is a question for the physicist and biologist instead of the chemist. The extension given to our command of low temperatures by the various forms of the modern ice-machine has increased the tendency to rely upon refrigeration as a disinfecting process, while experiments made upon the vitality of seeds of the higher orders of plants, after exposure to extraordinary cold, have not, so far as parallel inferences may be drawn from them, been by any means encouraging as to the destruction of the living organisms of simple structure whose important relation to the propagation of disease we have so much reason for believing to exist.

Among the chief steps of progress in recent years in regard to the industrial production of disinfecting materials, may be noted the great increase in the manufacture of phenol and cresol from coal tar (as also their sodium and calcium compounds), and their production in a state of far greater purity than formerly, the introduction upon a smaller, but still a commercial scale, of thymol and other of the higher phenols (the value of the special claims made in favor of which may still be considered open to discussion), the preparation in a very large way of salicylic acid by Kolbe's synthetic process, the manufacture of oxidized products from turpentine through which air is passed in the presence of water, the comparatively cheap production of the permanganates by the economical arrangements of Tessié du Motay and others, the use of bromine vapor, the manufacture of certain saline substances, such as aluminum chloride and bromide, in large quantity and at low price, with special advantages as to some details of their application, but of moderate or doubtful activity, and the supply of some new porous absorbents, such as Stanford's sea-weed charcoal, usefully available for some purposes of disinfection, within such distances from the seat of their production as are not too great to allow of moderate charges for transportation.

J. W. MALLET.

(*To be continued.*)

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

(Continued from p. 342.)

Metastasis.—By the term *Metastasis*, equivalent to the German "Stoffwechsel," we designate in general all those chemical changes in the constituents of the plant which are not accompanied by a production of organic matter. The metastasis of plants and of animals is very similar in its general character, while the "assimilation" of chlorophyl-bearing plants, that is, the production of new

organic matter, is peculiar to them, and radically distinct from the processes in the animal body to which the same name is applied.

Proteid Metastasis.—Our increased knowledge of the constitution of the albuminoids, due to the labors of Hlasiwetz and Habermann, Schützenberger and Kühne,* has not been without fruit in the domain of vegetable bio-chemistry, and has aided in forming some very probable conclusions regarding the chemical changes involved in the respiration of plants, and in the transfer of albuminoids from seed to sprout and from one part of the plant to another.

The first step in this direction was made by Pfeffer in his investigations into the functions of asparagine in the plant.† This substance, which is one of the products of the artificial decomposition of albuminoids by acids or by the digestive juices, is also found abundantly in seedlings of many plants, particularly leguminous plants. According to Pfeffer's investigations, asparagine, being soluble in water and diffusible, passes from the seed into the young plant and is there reconverted into albuminoids, and in this way the comparatively insoluble nitrogenous matters of the seed are transferred to the young plant where they are needed. Pfeffer experimented on germinating seeds of leguminous plants, and showed that, while the albuminoids were transferred to the young plant in the way just described, they appeared also to pass unchanged from seed to sprout.

It was also observed that the occurrence of asparagine in the seedlings corresponded exactly with that of glucose. Both were formed together in the radicle, the caulicle, the petioles of the cotyledons, and finally in the latter themselves; both were found in the parenchyma, but not in the vascular bundles, of the stem, and disappeared together before reaching the vegetation point.

These facts led to the conclusion that the presence of carbohydrates or other non-nitrogenous matters is necessary to the reconversion of asparagine into albuminoids, and the truth of this conclusion was established by later experiments. In these experiments‡ seedlings of *Lupinus luteus*, a plant which produces large quantities of asparagine, were grown in an atmosphere kept free from carbonic acid, and were thus limited to the small amount of non-nitrogenous matters furnished by the seed. Under these circumstances the plants grew until the reserve matters of the seed were exhausted, and at this time were found to contain large quantities of asparagine—much more than plants of the same age grown in presence of carbonic acid, and apparently about the same amount as plants grown in the dark. No glucose could be detected, and starch was found only in the guard-cells of the stomata.

At the time of Pfeffer's investigations asparagine was almost the only amide body whose presence in plants had been detected. Since that time, however, numerous other bodies of the same class

* See this Journal, 2, 204. † Jahrb. wiss. Botanik, 8, 530.
‡ Botanische Zeitung, 1874, 240.

have been discovered, among which may be especially mentioned two, which seem always to result from the decomposition of albuminoids, viz., leucine and tyrosine. These and other amides were found to be formed in varying quantities and proportions during the germination of many seeds, and to be contained in beets and potatoes, where they served as a reserve of nitrogenous food and were reconverted into albuminoids in the second year's growth.

These results led to a modification of Pfeffer's theory, inasmuch as they showed that asparagine was not the only nitrogenous product of the splitting up of albuminoids in the seed, but the main features of that theory remained unchanged.

Borodin* appears to have been the first to show conclusively that the occurrence of asparagine is not confined to seedlings and to roots and tubers. He found by micro-chemical investigations that asparagine was present in the leaf-buds of many trees and shrubs, and that in cases in which it was not normally present it could be developed by cutting off the twig bearing the buds and cultivating it in water, *i. e.* by depriving it of its supply of non-nitrogenous materials from the body of the plant. The occurrence of asparagine is not confined, however, to the leaf-buds. Borodin found that asparagine accumulated in the most various parts of the plant (stem, leaf-stalk, leaves, leaflets, flowers, etc.), when they were separated from the plant and cultivated in water. He also observed in many cases the occurrence of another body, which was most probably tyrosine, and of a third, undetermined body.

These results differ from Pfeffer's in one very important respect. They show that amides are formed not only when reserve stores of albuminoids are to be transferred to growing parts of the plant, but also in parts of the plant where, so far as we know, the only form of albuminoids present is the albumin of the living protoplasm. To account for this fact, Borodin supposes that in connection with the growth, or more probably with the respiration of the plant, a continual decomposition and regeneration of the albuminoids of the protoplasm takes place. The albuminoids, he believes, split up, yielding asparagine and other amides, and a non-nitrogenous residue, which combines with the oxygen of the air, forming carbonic acid and water. The amides formed in this process, together with the non-nitrogenous matters formed by assimilation or brought by diffusion from other parts of the plant, form the material for the regeneration of albuminoids, while, by virtue of their solubility and diffusibility, they readily serve to nourish protoplasm at a distance from the spot where they are formed.

On this theory the respiration of the plant, while it takes place at the expense of its non-nitrogenous ingredients, requires, as the first stage of the process, that their atoms become part of the molecules of the protoplasmic albuminoids. This assumption has much in its favor, and is accepted as probable by most authorities.

* Botanische Zeitung, 1878, 802.

Other observers have obtained results confirming those of Borodin. Kellner* found that numerous green fodder plants contain large quantities of non-albuminoid compounds, among which amides predominate, and also that these compounds are most abundant in young plants, while in those in which growth has nearly ceased they are largely converted into albuminoids.

Emerling† has investigated the distribution of amides in the bean plant (*Vicia faba maj.*), and has found, as the general result, that "those parts of plants which are actively growing and increasing their mass are richer in amides than older and more developed parts."

All these results are plainly in harmony with Borodin's theory, since they find the larger proportion of amides in those parts of plants where respiration and growth are most active, and where, according to that theory, they are most abundantly formed. It is true that it is in these parts of plants also that the amides are most actively regenerated to albuminoids; but in the first place it is a commonly observed fact that substances which serve as material for the formation of new tissue accumulate to a certain extent near the place where they are used, and in the second place, as we shall soon see, a modification of the theory which has been proposed by E. Schulze explains very simply the accumulation of amides in the growing parts of plants. Before passing to this, however, a few results obtained by Schulze‡ in experiments with twigs of birch and horse-chestnut cultivated in water, may be mentioned. In the leaves of both was found asparagine, and also indications of the presence of other amides. Indeed, a substance was separated from the twigs of the horse-chestnut which gave the reactions of leucine.

As just stated, Schulze has proposed certain modifications of Borodin's theory. In Schulze's first paper on the subject,§ which was published at about the same time as Borodin's paper, and independently of the latter, he propounded essentially the same views, but with considerable reserve. In his second article‖ he advances his theory with more positiveness and in greater detail. It is based on the facts already mentioned in this article, together with others, observed by himself and his co-laborers, regarding the proportions of the various amides found in plants and on their distribution in the plant.

He shows in the first place that while the decomposition of albuminoids in the plant yields, as already pointed out, essentially the same nitrogenous products as are produced by heating the albuminoids with acids and alkalies, the proportions in which the various amides are found in plants differ widely from those in which they are produced by the artificial decomposition of albuminoids.

For example, Schulze and Barbieri, in experiments on squash

* Landw. Jahrbücher, 8, 1 Supp. 243. † Landw. Versuchs-Stationen, 24, 113.
‡ Landw. Jahrbücher, 9, 713. § Ibid. 7, 411. ‖ Ibid. 9, 689.

seeds, determined as accurately as possible the quantities of the several amides produced in germination, and also in the artificial decomposition of the albuminoid of these seeds by hydrochloric acid and stannic chloride after the method of Hlasiwetz and Habermann. The results, from the nature of the case, are only approximate, but the observed differences are too great to be accidental. They were as follows:

	Germination. (Per cent. of dry matter of seedlings.)	Artificial decomposition. (Per cent. of protein used.)
Glutamic acid	1.75	3.4
Aspargic acid	0.06	2.5
Tyrosine	0.25	2.0
Leucine	trace	20.0

The proportions in which the various amides were found in the two cases are strikingly different.

So, too, in the germination of the legumes, large quantities of asparagine are observed with but little leucine, while the albuminoids of these seeds when treated with acid yield much leucine and but little asparagine. Many other similar examples are not wanting.

In the second place, Schulze has made some interesting and instructive observations on the distribution of amides in the seedling, experimenting chiefly on lupines. According to Pfeffer the asparagine of these seedlings originates in the cotyledons by the decomposition of their albuminoids, and passes from them to other parts of the plantlet. Schulze, however, found that the cotyledons of germinating lupines contained *less* asparagine than the remaining parts of the seedlings, a fact which it is difficult to explain on the assumption that the asparagine originates in the cotyledons and passes from them by osmose to other regions of the seedling. At the same time he found that the other amide-like bodies which accompany asparagine in germinating lupines were most abundant in the cotyledons.

It is worthy of note, also, that Pfeffer found that asparagine appeared first in the radicle, and last of all in the cotyledons.

The recent investigations into the constitution of the albuminoids have rendered it very probable that they contain as constituent groups of atoms the several amides which are found to result from their decomposition, and that the differences between the various albuminoids are at least partly due to differences in the proportions of the several amide groups which they contain. If this view be the true one, it is, as Schulze remarks, difficult to imagine that the same albuminoid should, under some circumstances, yield, *e.g.*, much leucine and little asparagine, and under other conditions much asparagine and little leucine. Yet this is exactly what appears to be the case with the conglutin of lupines, as we have just seen.

To explain this seeming anomaly, Schulze supposes, in the first place, that *some of the amides are more easily reconverted into albuminoids than others*. Thus, in the case just mentioned, he

supposes that the leucine resulting from the decomposition of the conglutin is a more available source of albuminoids to the plant than the asparagine, and that consequently the latter accumulates in the seedling. In the case of the squash, mentioned on p. —, it is the glutamine (or glutamic acid) which is least readily utilized in the plantlet, and which is consequently most abundant in it at any given time. In general those amides which are least easily reconverted into albuminoids are the ones which are most abundant.

This supposition alone, however, does not suffice to explain either the enormous accumulation of particular amides in certain cases or their peculiar distribution in the seedling already alluded to. For example, in lupine seedlings grown in the dark, as much as half of their total nitrogen has been observed to exist in the form of asparagine, while conglutin on treatment with acids or alkalies yields only about 2 per cent. of aspargic acid. Moreover, as we have seen, a larger proportion of this asparagine is found in the growing parts of the seedling than in the cotyledons where the decomposition of the conglutin must take place.

These facts lead most naturally to the further hypothesis that *an alternate formation and decomposition of albuminoids takes place* similar to the transitory starch building frequently noticed. This hypothesis permits us to consider the decomposition of albuminoids in the plant as analogous to, if not identical with, that occurring under the influence of acids and alkalies and of trypsin, and at the same time to explain the fact that the products of the decomposition are found in very different proportions in the two cases. Taking again the germination of the lupine as an illustration, our hypothesis supposes that the conglutin of the cotyledons first splits up into a mixture of leucine, tyrosine, asparagine, glutamine, etc. These amides are carried by diffusion to the growing parts of the plantlet, where they serve for the nutrition of the protoplasm of the cells and are reconverted into albuminoids. In this process those amides which are most easily reconverted are utilized first, while most of the asparagine seems to remain unacted on. The resulting albuminoids are supposed to be again decomposed into a mixture of amides which serve to nourish the protoplasm of remoter cells, while the asparagine is again left unassimilated. In this way, by repeated formations and decompositions of albuminoids, a considerable accumulation of asparagine might result *in the seedling*, while the cotyledons would naturally contain far less of it.

In later stages of growth the asparagine seems to be also assimilated and disappears, and in mature plants, where the vigor of assimilation is great, all the amides resulting from the decomposition of the protoplasmic albuminoids in respiration are rapidly reconverted into albuminoids, and can sometimes be detected only by cutting off the supply of non-nitrogenous materials, as in Borodin's experiments.

The theory which has been developed in the foregoing pages explains equally well the facts observed in seedlings and the results

obtained by Borodin on mature plants, and presents them to us as different phases of the same phenomenon; it is in accordance with Borodin's conclusions concerning the respiration of plants; and finally it throws some light on Pfeffer's observation that the cells of the vascular bundles in the stems of germinating lupines and other legumes are rich in albuminoids, which, according to this theory, were formed from amides and serve in turn as the source for further production of amides.

To recapitulate briefly, the theory assumes that the production of amides in the plant (except from the reserve albuminoids of the seed, if such a production takes place) is a normal function of the living protoplasm and part of the process of respiration. The oxygen of the air unites with the non-nitrogenous residue of the protoplasm, producing carbonic acid and water, while the fate of the amides depends upon the supply of non-nitrogenous matters. If this is abundant, as in mature plants, a rapid regeneration of albuminoids takes place, and little or no residue of amides can be detected. When the supply of non-nitrogenous matters is less abundant, as in germination, or when it is artificially suppressed, only those amides which are most easily reconverted into albuminoids suffer this change, the others accumulating to an extent depending on the amount of non-nitrogenous matter supplied and on the opportunity for assimilation. In any case those amides which are utilized are combined with non-nitrogenous matter and become part of new protoplasm, situated perhaps at a distance from the source of the amides, ready to be again decomposed in the same way. Thus the respiration of the plant, while taking place at the expense of non-nitrogenous substances, is performed by the protoplasm, and incidentally, so to speak, produces soluble and diffusible nitrogenous compounds for the nourishment of other protoplasm.

The theory described in the above paragraphs regards the amides solely as products of the regressive changes of the albuminoids. In the case of plants which have passed beyond the stage of dependence on the reserve matters of the seed, another view is possible, viz., that they are intermediate products in the formation of albuminoids from inorganic nitrogen compounds. This view is a very plausible one, but is difficult of proof. It is certain that amides are formed from albuminoids in the plant, and are reconverted into them, and it is difficult, if not impossible, to say in any given case that the amides whose presence is observed cannot have had their origin in albuminoids and must have been derived from nitric acid or ammonia. Consequently, while bearing in mind the possibility of such a source for some of the amides, we cannot yet go beyond the acknowledgment of its possibility, while the functions of the amides in the translocation of albuminoids are, in their main features, well established.

H. P. Armsby.

NOTES.

Properties of Ozone.

HAUTEFEUILLE and CHAPPUIS are carrying on an investigation of ozone, more particularly of its physical properties, and have already reached results of interest. With a view to obtaining a mixture rich in ozone, they first study * the influence of pressure and temperature on the formation of ozone from oxygen by means of electrical discharge. Their results show that the tensions of transformation are not a function of temperature alone, but also of pressure; hence the equilibrium between oxygen and ozone can not be analogous to that which is established in the decompositions of fixed combinations, and in the production of saturated vapors from solids or liquids. Their figures show, however, that the ratio of the volume of ozone to the volume of the whole mixture is nearly independent of pressure within considerable limits, and hence that there is an analogy between the transformation of oxygen under electrical influence and the dissociation of gases; for in the case of hydriodic acid, and others, at certain temperatures, the dissociation is limited by tensions sensibly proportional to the total pressure. The proportion of hydrogen and iodine liberated increases as the pressure diminishes, so also the proportion of oxygen to ozone. The combination of hydrogen and iodine and the transformation of oxygen into ozone, both absorbing heat, should then be favored by an increase of density.

To obtain therefore a mixture rich in ozone,† they allowed oxygen to remain for one-quarter of an hour in the apparatus for alternating discharges, the latter being plunged in methyl chloride to produce a low temperature. The gas was then passed into the reservoir of Cailletet's condensing apparatus, previously exhausted and reduced to —23°. They were thus enabled in one and a quarter hours to fill the reservoir with a mixture containing a large proportion of ozone. This was then compressed by mercury at 0°, the reservoir being kept at —23°. The mercury was not acted upon by the gas as much as was anticipated, but the treating by compression gave greater difficulty. However, they succeeded in obtaining a high tension. At the first stroke of the piston the capillary tube showed an azure blue color which increased with increase of pressure. When the pressure reached several atmospheres the color of the gas was indigo blue, and that of the meniscus of mercury seen through the glass tube was steel-blue. The color disappeared when the tension

* Comptes rendus, July 26th, p. 228. † Ibid. Sept. 20th.

was lessened. Sudden expansion after a pressure of seventy-five atmospheres caused a thick fog, a certain sign of liquefaction or even solidification which is reached with oxygen only after a pressure of three hundred atmospheres.

A comparative study of mixtures of oxygen and ozone and oxygen and carbon dioxide showed that ozone is a little less easily liquified than carbon dioxide. The mixture of oxygen and ozone must be cooled when compressed, or heat is generated and a strong detonation follows accompanied by heat and yellow light. Berthelot has shown that the heat of formation of ozone is —14.8 cal. for $O_3 = 24$, and the experiments of Hautefeuille and Chappuis show that it is also explosive. This fact can be partly observed at ordinary temperature; for if the gas obtained from the electrical apparatus be passed into a capillary tube placed in water at 25° and rapidly compressed, ozone is often destroyed with explosion. If the same is maintained at —23° and ten atmospheres of pressure, it can be kept for hours, if separated from the mercury by a layer of sulphuric acid. The azure blue color can be seen in this case almost as well as in the first, it being perceptible in a tube 1 mm. in diameter in the dimly lighted room of the Ecole Normale. The color is as characteristic of ozone as its odor, being visible at all tensions if the gas be in sufficiently thick layer. It can be seen by holding between the eye and some white surface a tube 1 meter long through which passes a current of oxygen from Berthelot's electrical apparatus.

The same investigators next study the effect of certain gases on the transformation of oxygen into ozone.* They find that the presence of a very small quantity of chlorine prevents the formation of ozone, or destroys it after it is formed. The presence of nitrogen increases the proportion of ozone formed at low pressure by nearly one-half. With hydrogen for the same temperature and tension of oxygen, the proportion of ozone is greater than with nitrogen. With fluoride of silicon the proportion reaches even .40; but in this case the form of discharge changes. In order to furnish comparable results the form of discharge as well as the temperature should remain the same.

They next endeavored to obtain ozone as a permanent liquid.† At two hundred atmospheres and —23° the gas was blue, but no liquid appeared. A part of the tube was then reduced to —88° and the color appeared three or four times as intense as at —23°. The mercury was frozen and unacted upon by the ozone, but there was no liquefaction. A large proportion of carbon dioxide was then added to the mixture. At —23° and with slow increase of pressure a liquid appeared colored blue, the same as the gas above it. This liquid was permanent while the pressure continued, being a solution of ozone in liquid carbon dioxide. Although unsuccessful so far in their attempts to obtain liquid ozone, they hope to succeed by

* Comptes rendus, Nov. 8th, p. 762. † Ibid. Nov. 15th.

compressing at low temperature a mixture of oxygen and ozone obtained at —88° and containing more than 50 per cent. of ozone.

The appearance of color enabled them to show the large proportion of ozone in the mixture obtained by submitting carbon dioxide to the electrical discharge, thus confirming the supposition that the high oxidizing power of this mixture observed by Berthelot is due to ozone rather than to a percarbonic acid.

As the blue color of ozone recalled that of the sky, Chappuis* undertook to compare the absorption spectrum of the former with the atmospheric absorption bands and found several coincidences, but at his last report had not completed the study.

A. V. E. Y.

On new Ethers of Carbonic Acid.

In the last number of this Journal attention was called to an investigation by Ludwig Schreiner which led to the remarkable conclusion that there are two isomeric substances of the formula $CO\begin{cases}OCH_3\\OC_2H_5,\end{cases}$ and also two substituted ureas $CO\begin{cases}NH.C_2H_5\\NH.CH_3\end{cases}$. The results of Schreiner would of course necessitate the abandonment of the now commonly accepted view regarding the equivalence of the four affinities of carbon. Almost immediately after the publication of Schreiner's paper, there appeared another on the same subject by Röse, working in Geuther's laboratory. Strange to say, however, the results reached by Röse are exactly the opposite of those reached by Schreiner. Röse describes a number of new ethers of carbonic acid, including such as contain only one kind of residue, and such as contain two kinds. The methylethyl ether, whether prepared by first introducing methyl and then ethyl, or in the opposite way, was found to have exactly the same properties. The same is true of the methylpropyl, methylbutyl, ethylbutyl and ethylamyl ethers. The boiling points, specific gravities and refractive indices of the members of each pair of isomerides are found to be exactly the same. Further investigation will be necessary to decide which of the two investigators is in the right. As the matter is one of fundamental importance, it is desirable that it should be definitely cleared up as soon as possible.—(*Annalen der Chemie*, 205, 227.)

The Atomic Weight of Glucinum.

NILSON has replied to Lothar Meyer on the subject of the atomic weight of glucinum. Meyer attempted to show that the most natural conclusion to be drawn from the experiments of Nilson and Pettersson is that the atomic weight of this element is 9.1, as has hitherto been assumed. Nilson, however, calls attention to certain facts which Meyer apparently lost sight of, and which put quite a different light on the matter. The molecular heats of the oxide of glucinum and the sulphate are those which the theory requires on

*Comptes rendus, Dec. 13th.

the supposition that the compounds have the formulas Be_2O_2 and Be_2SO_4. The values found correspond to those for the oxide and sulphate of aluminum. If the oxide of glucinum has the formula Be_2O_2, then the element has the atomic weight 13.65, or exactly half the atomic weight of aluminum. — (*Ber. d. deutsch. chem. Gesell.* 13, 2035.)

Synthesis of Tropic Acid.

LADENBURG and RÜGHEIMER have achieved a brilliant success in their studies upon the alkaloids. They have previously shown that hydratropic, atrolactinic, atropic and tropic acids can be transformed one into the other. The synthesis of any one of the first three acids would hence lead to that of tropic acid itself. They have now succeeded in building up atropic acid. For this purpose they start with acetophenone, $C_6H_5CO.CH_3$. This is converted into dichlorethylbenzene $C_6H_5CCl_2CH_3$ by treating with phosphorus pentachloride. The chloride is then warmed with an alcoholic solution of potassium cyanide, when the following reaction takes place:

$$C_6H_5CCl_2CH_3+KCN+C_2H_5OH=C_6H_5C\begin{cases}CH_3\\OC_2H_5\\CN\end{cases}+KCl+HCl.$$

Now, on boiling the product with baryta-water the cyanide is converted into the corresponding acid thus:

$$C_6H_5-C\begin{cases}CH_3\\OC_2H_5\\CN\end{cases}+ba(OH)+H_2O=C_6H_5-C\begin{cases}CH_3\\OC_2H_5\\COOba\end{cases}+NH_3.$$

The acid formed is ethylatrolactinic acid. When treated with hydrochloric acid it readily yields atropic acid, $C_6H_5-C\begin{cases}=CH_2\\COOH;\end{cases}$ and this acid may be converted into tropic acid by first adding hypochlorous acid and replacing by means of hydrogen the chlorine of the product, the reactions being:

$$C_6H_5-C\begin{cases}CH_2\\COOH\end{cases}+HOCl=C_6H_5-CCl\begin{cases}CH_2OH\\COOH\end{cases}$$

and $$C_6H_5-CCl\begin{cases}CH_2OH\\COOH\end{cases}+H_2=C_6H_5-CH\begin{cases}CH_2OH\\COOH\end{cases}+HCl.$$

Tropic acid.

—(*Ber. d. deutsch. chem. Gesell.* 13, 2041.)

On the Hydrocarbons of American Petroleum.

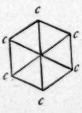
The results recently reached by BEILSTEIN and KURBATOW in their examination of the petroleum from the Caucasus, a brief account of which was given in the last number of this Journal, have led the authors to examine American petroleum. By means of

fractional distillation heptane was separated from petroleum. It boiled at 95–100° and had the specific gravity 0.7192. The analysis showed that the substance contained a slightly larger amount of carbon and smaller amount of hydrogen than the formula C_7H_{16} requires. This heptane was heated with four parts of ordinary nitric acid (sp. gr. 1.38) as long as nitrous fumes were given off. From the layer of oil floating on the acid at the end of the operation, heptane was again isolated. It was found to boil at 98.5–99.5°, and has the specific gravity 0.6967. The analyses now gave results in accordance with the formula C_7H_{16}. This perfectly pure heptane is not attacked materially by nitric acid.

It is thus shown that besides the hydrocarbons C_nH_{2n+2}, there are other hydrocarbons, containing less hydrogen, in American petroleum. Crude heptane had a higher specific gravity, contained less hydrogen than the formula C_7H_{16} requires, and was attacked by nitric acid.

It seemed probable that American petroleum might contain the same addition products of the benzene hydrocarbons as were found in Caucasian petroleum. On treating that portion of the American variety which boils between 115° and 120°, with a mixture of concentrated nitric and sulphuric acids, a small quantity of *trinitroisoxylene* was obtained. Hence it is seen that, besides the hydrocarbons C_nH_{2n+2}, American petroleum contains others of the general formula C_nH_{2n}.—(*Ber. d. deutsch. chem. Gesell.* 13, 2028.)

Concerning the Formula of Benzene.

In a recent paper on thermochemical investigations on hydrocarbons, JULIUS THOMSEN drew the conclusion that the commonly accepted formula of Kekulé for benzene is incorrect, and that the formula  is more probable. At the same time Brühl concludes from his investigations that Kekulé's formula is correct. Brühl bases his conclusion on the fact that the molecular refraction of benzene is that which, according to his rule, a substance with three double links would require. To this THOMSEN now replies. He says: "The molecular refraction is considered as an expression of the density of the body, and the conclusion is hence drawn that, if the body has a higher molecular refraction than the normal, calculated from its elements, this indicates a greater density which is caused by a stronger linking of the carbon atoms of the body; and the conclusion is further drawn that this greater density of benzene can be explained by assuming three double linkages.

"The explanation of the greater density may be just as easily and consistently explained in another way. According to the theory, a linking of the six carbon atoms by six single links would give the normal density and the normal molecular refraction; each carbon atom would then be in combination with two others. But the six

carbon atoms still have six affinities, which can give three single linkages. If these three affinities are employed to unite each carbon atom with three others, then, if the linkages have any influence on the density, a linking of *each* carbon atom to three other carbon atoms must necessarily cause a greater density than would be caused by union of each carbon atom with only two others.

"The supposed greater optical density, *i.e.*, the increased molecular refraction of benzene, may hence be explained just as easily by assuming the presence of nine single links, which unite each carbon atom with three others, as by assuming three double links." —(*Ber. d. deutsch. chem. Gesell.* 13, 2166.)

Arsinobenzoic Acid.

La Coste has oxidized tolylarsinic acid, $C_6H_4\begin{cases}CH_3\\AsO(OH)_2\end{cases}$, and obtained a substance which he calls benzarsinic acid, $C_6H_4\begin{cases}COOH\\AsO(OH)_2\end{cases}$. When benzarsinic acid is heated, it gives off water, and the anhydride is formed. This is *arsinobenzoic acid*, $C_6H_4\begin{cases}COOH\\AsO_2\end{cases}$, a compound analogous to nitrobenzoic acid, and differing from the latter only in the fact that it contains the element arsenic in the place of nitrogen.—(*Ber. d. deutsch. chem. Gesell.* 13, 2176.)

Baeyer's Method for the Synthesis of Indigo.

Baeyer describes two processes for the synthetic preparation of indigo, both of which start from cinnamic or phenylacrylic acid $C_6H_5.CH.CH.CO_2H$.

In both processes nitrogen is introduced into the molecule in the form of NO_2 in the phenyl. Only the ortho-nitro acid is capable of forming indigo. Orthonitrocinnamic acid being prepared, Baeyer transforms it into orthonitropropiolic acid or into orthonitrophenyloxyacrylic acid by processes identical with those which are employed for transforming cinnamic acid into phenylpropiolic acid or into phenyloxyacrylic acid. The two ortho-nitro acids are transformed into indigo by simple reactions. The different steps in the synthesis are these:

1. *Preparation of orthonitrophenylpropiolic acid.*—Orthonitrocinnamic acid is brominated; there is formed $C_6H_4(NO_2).C_3H_3Br_2O_2$. Boiling alcoholic solutions of the alkalies extract 2HBr from this body; there remains $C_6H_4(NO_2)(C_3HO_2)$, orthonitrophenylpropiolic acid.

2. *Preparation of orthonitrophenyloxyacrylic acid.*—Orthonitrocinnamic acid is treated with chlorine, when orthonitrophenylchlorolactic acid is formed.

$$C_6H_4(NO_2)—CH=CH—COOH+HClO=$$
$$C_6H_4(NO_2)—CH(OH)—CHCl—COOH.$$

When this acid is treated with caustic alkalies in solution, it loses the elements of hydrochloric acid, and is transformed into orthonitrophenyloxyacrylic acid.

$$C_9H_4(NO_2)—CH(OH)—CHCl—COOH=HCl+C_6H_4(NO_2)—C(OH)=CH—COOH.$$

3. *Preparation of indigo.*—The action of heat alone converts orthonitrophenyloxyacrylic acid into indigo.

$$C_9H_7NO_5=C_8H_5NO+CO_2+H_2O+O.$$

The reaction takes place at 110° C. The yield by this method is not good.

With orthonitrophenylpropiolic acid the process takes place more regularly. It requires the simultaneous action of an alkali and a reducing agent.

$$C_9H_5NO_4+H_2=C_8H_5NO+CO_2+H_2O.$$

Baeyer recommends the use of a mixture of glucose and an alkaline carbonate. The transformation takes places at 110° and the indigo separates in crystalline form. Baeyer much prefers the latter to the former method. It presents a peculiarity which deserves special notice: it is that the reaction can be brought about directly by the fabric.

The textile fiber is impregnated with a mixture composed of orthonitrophenylpropiolic acid, an alkaline substance and a solution of glucose, when it is exposed to the desired temperature, for example, in a current of superheated steam. The indigo blue will be produced in the material, and will be intimately fixed on the fiber.

If artificial indigo should be too expensive to replace the natural product in the processes of dyeing, it might still be that its formation directly on the fiber could be of advantage. Its use will depend less on its price than on the regularity of its formation.—(M. Rosenstiehl in *Annales de Chimie*, 21, 286; and *Ber. d. deutsch. chem. Gesell.* 13, 2254.)*

Dr. FERD. FISHER has undertaken the editing of the *Jahresbericht für die chemische Technologie*, succeeding Prof. von Wagner, who recently died. Dr. Fisher has for a long time past edited *Dingler's Polytechnisches Journal.*

Professor B. C. BRODIE, Bart., F. R. S., D. C. L., the eminent English chemist, died November 24, 1880. He was born in London in 1817. He studied under Liebig at Giessen, and undertook his first investigation there in 1845. From this time he was actively engaged in research. In 1855 he was appointed Professor of Chemistry in the University of Oxford. In 1866 he published his

*The original paper of M. Rosenstiehl contains a number of serious errors. In the above abstract these have been corrected.—ED.

"Calculus of Chemical Operations," in which he puts forth novel views respecting the nature of chemical change.

Dr. WILLIAM HEINTZ, Professor of Chemistry at the University of Halle, died recently at the age of sixty-three years.

Dr. JOHN STENHOUSE, F. R. S., the well-known English chemist, died December 31. He held at one time the lectureship in chemistry in St. Bartholomew's Hospital, London. In 1865 he succeeded Dr. Hofmann as non-resident assayer to the Royal Mint.

A Cincinnati Chemical Society has just been organized, with the following officers: President, F. W. Clarke; Vice President, F. Roeder; Secretaries, W. L. Dudley and Alfred Springer; Treasurer, H. F. Reum. Monthly meetings will be held, for the reading of papers, and discussion.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

ARMSBY, H. P. Manual of Cattle-Feeding: a Treatise on the Laws of Animal Nutrition and the Chemistry of Feeding-Stuffs in their Application to the Feeding of Farm Animals. New York: Wiley. $2.50.

COOKE, J. P. Religion and Chemistry: a Re-statement of an old Argument. Newly revised edition. New York: Scribner. $1.50.

DOUGLAS, S. H., and PRESCOTT, A. B. Qualitative Chemical Analysis. 3d edition revised. New York: Van Nostrand. $3.50.

LEGG, J. W. Guide to the Examination of Urine. 5th edition. Reprint. Philadelphia: P. Blakiston. 75 cents.

SEMPLE, C. E. A. Aids to Chemistry. Cloth, 50 cents; paper, 25 cents. Reprint. New York: Putnam.

MUTER, J. Introduction to Pharmaceutical and Medical Chemistry. New edition. Reprint. Philadelphia: Blakiston. $6.00.

II.—ENGLISH.

ARMSTRONG, H. E. Introduction to the Study of Organic Chemistry. 2d edition. London: Longmans. 3s. 6d.

BRODIE, B. C. Ideal Chemistry. London: Macmillan. 2s.

MILLER, W. A. Elements of Chemistry, Theoretical and Practical. Part 3. Chemistry of Carbon Compounds, or Organic Chemistry. Section 1. 5th edition. London: Longmans. 31s. 6d.

MORRIS, D. A Class-book of Inorganic Chemistry. New edition. London: Philip. 2s. 6d.

ROSS, W. A. Alphabetical Manual of Blowpipe Analysis. London: Trübner. 5s.

ROSS, W. A. Pyrology, or Fire Chemistry. London: Trübner. 36s. New ed.

WILLS, T. The Life of Thomas Wills, Demonstrator of Chemistry, Royal Naval College, Greenwich. By his Mother, Mary Wills Phillips, and J. Luke. Nisbet. 3s. 6d.

WURTZ, A. The Atomic Theory. Translated by E. Cleminshaw. London: Paul. 5s.

III.—FRENCH.

CHAPINS, A. Role chimique des ferments figurés. Baillière. 3fr. 50.

GORUP-BESANEZ. Traité de chimie physiologique. Traduit et annoté par F. Schlagdenhauffen. 2 vol. Dunod. 32fr.

LACOTE, A. Synthèse des corps azoté. Baillière. 2fr. 50.

MAUMENÉ, E. J. Théorie générale de l'action chimique. Dunod. 9fr.

PISANI, F. Traité pratique d'analyse chimique qualitative et quantitative. G. Baillière. 3fr. 50.

SCHÜTZENBERGER, P. Traité de chimie générale, comprenant les principales explications de la chimie aux sciences biologiques et aux arts industriels. Tome II. Hachette. 14fr.

WALLACH, O. Tableaux servant à l'analyse chimique. Traduit par J. Krutwig. Reinwald. 2fr. 50.

IV.—GERMAN.

ARENDT, R. Technik der Experimentalchemie. 1 Bd. 1, 2 Lief. Leipzig: Voss.

AUERBACH, G. Das Anthracen und seine Derivate. 2 vermehrte Aufl. Braunschweig: Vieweg u. Sohn. M. 7.20.

BEILSTEIN, F. Handbuch der organischen Chemie. 1 Lief. Leipzig: Voss. M. 3.

BELOHOUBEK, A. Ueber den Einfluss der geologischen Verhältnisse auf die chemische Beschaffenheit d. Quell- und Brunnenwassers. Prag: Rziwnatz. M. 1.20.

BERSCH, J. Die Essig-Fabrikation. 2 Aufl. Wien: Hartleben. M. 3.

BUNSEN, R. Flammenreactionen. Heidelberg: Koester. M. 1.

DUMREICHER, O. Untersuchungen über die Einwirkung von Zinnchlorür auf die Stickstoffsauerstoffverbindungen. Wien: Gerold's Sohn. M. 0.50.

ELSNER, F. Die Praxis d. Nahrungsmittel-Chemikers. Leipzig: Voss. M. 4.

FISCHER, F. Die chemische Technologie des Wassers. Braunschweig: Vieweg. M. 11.60.

FISCHER, F. Leitfaden der Chemie und Mineralogie. Hannover: Hahn'sche Buchh. M. 2.80.

FALCK, F. A. Lehrbuch der praktischen Toxikologie. Stuttgart: Enke. M. 8.

GERBER. Chemisch-physikalische Analyse der verschiedenen Milcharten und Kindermehle. Bremen: Heinsius.

GODEFFROY, R. Compendium der Pharmacie. 1, 2 Lief. Wien.

GROSS, G. Die Stickstoffgruppe der neueren Chemie und die der Atomen ihrer Elemente zuzuschreibende Valenz. Hamburg: Jenischen. M. 1.

GROSSE-BOHLE, A. Ueber das optische Verhalten d. Senarmontits und der regulären arsenigen Säure. Lüdinghausen: Rademann. M. 2.

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Vol. II. p. 348, line 16 from top read 43550 for 550.